Topical Review

Directed self-assembly of block copolymers for sub-10 nm fabrication

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Abstract
Directed self-assembly (DSA) emerges as one of the most promising new patterning techniques for single digit miniaturization and next generation lithography. DSA achieves high-resolution patterning by molecular assembly that circumvents the diffraction limit of conventional photolithography. Recently, the International Roadmap for Devices and Systems listed DSA as one of the advanced lithography techniques for the fabrication of 3–5 nm technology node devices. DSA can be combined with other lithography techniques, such as extreme ultra violet (EUV) and 193 nm immersion (193i), to further enhance the patterning resolution and the device density. So far, DSA has demonstrated its superior ability for the fabrication of nanoscale devices, such as fin field effect transistor and bit pattern media, offering a variety of configurations for high-density integration and low-cost manufacturing. Over 1 T in \( -2 \) device density can be achieved either by direct templating or coupled with nanoimprinting to improve the throughput. The development of high \( \chi \) block copolymer further enhances the patterning resolution of DSA. In addition to its superiority in high-resolution patterning, the implementation of DSA on a 300 mm pivot line fully demonstrates its potential for large-scale, high-throughput, and cost-effective manufacturing in industrial environment.

Keywords: directed self-assembly, lithography, nanofabrication, sub-10 nm, block copolymer

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

1. Introduction

Moore’s law, which predicts that the number of transistors doubles every two years, has guided the semiconductor industry for decades. However, in recent years, the validity of Moore’s law has been doubted as continued shrinking of device size necessitates sub-10 nm design rules. New directions have been proposed as an extension of Moore’s law in the International Technology Roadmap for Semiconductor (ITRS), such as More Moore and More than Moore. More Moore focuses on the innovation of device structure, materials, and fabrication techniques to maintain the trend predicted by Moore’s law. Conversely, More than Moore is more application driven with an emphasis on functional integration instead of simply scaling of device feature size [1]. Despite the competing focuses of the technological alternatives, the continuous advancement of nanofabrication techniques plays a crucial role for enhancing the performance of future devices. To achieve this goal, tremendous efforts have been made in developing lithography techniques, the critical step in nanofabrication that determines the minimum attainable pitch size.

The ITRS lists several potential techniques for next generation lithography, including extreme ultra violet (EUV) lithography, double (or quadruple) patterning, and directed self-assembly (DSA) of block copolymers (BCPs). Among these
techniques, large scale implementation of EUV is delayed but expected in a few years, but at a very high cost [2]. While double (or quadruple) patterning may alleviate the pressure of developing new lithography processes with shorter wavelength, this technique ultimately increases the cost of nanofabrication and the difficulty of aligning multiple masks [3]. Electron beam lithography (EBL) effectively produces custom patterns with sub-10 nm resolution without a mask, but is limited by relatively low throughput even with multi-beam configurations [4, 5]. Comparatively, DSA of thin films of BCPs is a cost-effective patterning methodology with a resolution comparable with EUV and EBL. This technique relies on the ability of BCPs to self-assemble into nanoscale structures of various morphologies. The driving force of self-assembly of BCPs is the thermodynamic incompatibility of its constituent blocks, which separates the BCPs into domains that are limited to nanoscale dimensions because of the covalent link between the blocks in each BCP molecule [6]. However, applying BCP self-assembly to nanofabrication requires additional stimuli, such as a chemically modified neutral substrate or a pre-deposited guide pattern in order for the BCPs to self-assemble into a desirable oriented, periodic structure. The ability to guide the self-assembly of a BCP is referred to as DSA [7]. The International Roadmap for Devices and Systems (IRDS) considers DSA, in combination with EUV, as a next generation patterning technique (figure 1) [8].

In 1995, Mansky et al reported the first demonstration using a BCP for lithography. They used polystyrene-block-polybutadiene (PS-b-PB) to form a spherical microdomain structure after annealing. The annealed structure was selectively etched to obtain arrays of hexagonal spots [9]. In 1997, Russell’s group obtained a substrate that was non-preferential to BCP blocks through chemical modification. As a result, the BCP could self-assemble into lamellae or hexagonal arrays of cylinders oriented perpendicular to the underlying substrate [10]. Another concern for BCP-based lithography is to form a long-range-ordered nanostructure. Two DSA methods were proposed to solve this problem: graphoepitaxy and chemo-epitaxy. Graphoepitaxy was originally presented by Kramer and coworkers, who utilized lithographically pre-patterned topographical patterns to direct the assembly of BCPs [11]. Kim and Nealey et al introduced chemo-epitaxy, another effective method to direct BCP self-assembly on a chemically pre-patterned substrate [12]. Both methods can achieve a density multiplication comparable to the original lithography-created pattern. Polystyrene-block-poly-poly (methyl methacrylate) (PS-b-PMA) is one of the most comprehensively studied BCPs to date. PS-b-PMA has been widely used for generating various long-range, periodic nanostructures (e.g. lamellar, spherical, cylindrical, and angled structures). PS-b-PMA can easily form a perpendicularly oriented, through-film structure on a non-preferential substrate due to the almost equal surface energies of the PS and PMMA blocks. The two blocks in PS-b-PMA also exhibit a selectivity difference during dry etching, enabling the PS block to act as a mask for pattern transfer after etching. However, PS-b-PMA has a relatively low Flory-Huggins interaction parameter (χ of 0.04), which restricts its minimum attainable pitch size to about 22 nm [13].

The fact that the miniaturization of device feature size will gradually reach the sub-10 nm era has motivated several research groups to explore the capability of DSA in the sub-10 nm field. One direction involves exploring new BCPs with high χ to obtain sub-10 nm half-pitch size. One category of high χ BCPs contains inorganic components, such as silicon- or iron-containing block. Some examples of silicon-containing BCPs include polystyrene-b-polydimethylsiloxane (PS-b-PDMS), polystyrene-b-poly(trimethylsilylstyrene) (PS-b-PTMSS), and polystyrene-b-poly(pentamethyldisilystyrene) (PS-b-PPDSS) [14]. Fully organic BCPs can also form sub-10 nm features. For instance, polystyrene-b-poly(2-vinyl pyridine) (PS-b-P2VP) and polystyrene-b-poly(propylene carbonate) (PS-b-PPC) have shown sub-10 nm patterning resolution [15, 16]. Even though employing a high χ BCP can minimize the pitch size of the obtained nanostructure, thermal annealing is impossible due to the substantial surface energy incompatibility of the constituent blocks. Without annealing the BCP cannot form a stable, ordered, through-film perpendicularly morphology. Therefore, different methods have been proposed to compensate for the difference in surface energies. For instance, solvent annealing at room temperature has been used in place of thermal annealing for many high χ BCPs [17–19]. Alternatively, a non-preferential top-coat layer, with a range of chemistries, has been applied to assist BCPs in forming through-film perpendicular structures on non-preferential substrates [20]. Combinations of different technologies have also been explored to process high χ BCPs [21].

Given the academic achievement in DSA research, the compatibility of DSA technology with existing industrial fabrication processes has become a significant concern in semiconductor industry. Researchers at the IMEC carried out pilot-scale runs on 300 mm wafer fabrication line to understand the process conditions and defectivity level of DSA lithography. These experiments covered line/space patterning with chemo-epitaxy and graphoepitaxy processes on PS-b-PDMA (14 nm half-pitch). It was found that DSA can be successfully adapted to the current 300 mm fabrication line within a satisfactory process window [22]. The screened defects with known causes were significantly reduced to a much lower level. It was also observed that hole shrinking as a potential application of DSA could be achieved with the same settings [23]. The results of these experiments further increased the chances of DSA industrialization.

Regardless of the research efforts in developing DSA technology, there are still several challenges to overcome before full industrialization of DSA can be made possible. Material availability will be the first concern because supplying large quantities of high χ BCPs has yet to be realized. As the pitch size of high χ BCPs decreased to a few nanometers, the size of the guide pattern will also become smaller. This may result in tighter process windows compared with the current PS-b-PDMA system. Meanwhile, implementing high χ BCPs requires new processing conditions, such as applying solvent annealing or a top-coat layer. Fabrication may become more complex after increasing the number of processing steps.
or incorporating additional processing tools and chemicals. Furthermore, effective imaging tools are needed for defect inspection and defect prevention strategies need to be made based on a thorough study of high $\chi$ BCPs systems.

In this review, we will focus on discussing DSA technologies for sub-10 nm patterning, with focuses on recent research on BCPs with high $\chi$, and the corresponding processing methods and conditions. Various methods for pattern transfer will be summarized and compared. Additionally, we will review important opportunities and obstacles for industrial implementation and application of DSA.

### 2. High $\chi$ BCPs and process control

The application of DSA in high resolution lithography largely depends on the intrinsic properties of BCPs. One of the most important properties of a BCP is the incompatibility between its component blocks, characterized by the Flory-Huggins interaction parameter $\chi$. For the past decade, PS-$b$-PMMA has been the most commonly used BCP for DSA studies, because the two blocks maintain similar surface energies over a broad temperature range. As a result, the orientation of the domains on the surface of PS-$b$-PMMA are easily controllable [24]. Additionally, the natural etch selectivity between PS and PMMA allowed for simple mask preparation for pattern transfer. Unfortunately, the low $\chi$ value of PS-$b$-PMMA limits nanopatterning to features larger than 10 nm, as reported by Wan et al [25]. Numerous efforts have been made to synthesize BCPs with $\chi$ values larger and similar properties to PS-$b$-PMMA for DSA. In this chapter, we will review the development of high $\chi$ BCPs in recent years and the exploration of necessary processing conditions for treating high $\chi$ BCPs, such as solvent vapor annealing (SVA) and top-coat methods.

#### 2.1. Emerging high $\chi$ BCPs

Generally, high $\chi$ BCPs refer to BCPs that have highly incompatible blocks. This property is determined by the domain spacing, $L_0$, ($L_0 \approx \chi^{1/6} N^{2/3}$, $L_0$ is full pitch size, N is degree of polymerization) in BCPs, which directly determines the ultimate feature size ($\sim 0.5 L_0$) of the obtained patterns [20]. Lowering N reduces $L_0$. Usually, microphase separation of BCP happens when $\chi N > 10.5$, therefore, when N decreases, $\chi$ must increase to satisfy the microphase separation condition. The $\chi$ value also affects the interfacial width between two domains. Higher $\chi$ usually results in a smaller interfacial width and decreases line-edge roughness [26, 27]. Two broad types of high $\chi$ BCPs have been extensively explored: BCPs containing inorganic blocks and fully organic BCPs. BCPs containing inorganic blocks show a high etch contrast between their blocks that facilitates pattern transfer. There are a number of processing friendly, fully organic BCPs that can be thermally annealed to assemble ordered structures. Their properties and performance will be discussed in more detail.

##### 2.1.1. High $\chi$ BCPs with all organic blocks.

Recent years have witnessed the synthesis and assembly of a number of fully organic high $\chi$ BCPs with domain sizes smaller than 10 nm. We will review the recent progress in synthesizing several types of novel fully organic high $\chi$ BCPs, which can be assembled by thermal annealing.
opening polymerization method. The advantages of incorporating a polycarbonate block include the capability of increasing the χ value and flexibility in selecting etching methods [28]. The χ value of the as-synthesized BCP can be easily tuned by altering the chemical composition of the polycarbonate block [29]. Moreover, the polycarbonate block allows both dry and wet etching, effectively increasing the etch selectivity between the two blocks, which is beneficial for subsequent pattern transfer. So far, polycarbonate based BCPs have been proposed as a potential replacement for PS-b-PMMA. An IBM research group demonstrated the formation of perpendicularly orientated cylindrical domains through simple thermal annealing (figure 2) [30].

2.1.1.2. Polystyrene-block-poly(propylene carbonate) (PS-b-PPC). PS-b-PPC is another example of a polycarbonate-based BCP, with an χ value of 0.079 (150 °C) and L0 less than 20 nm. It is synthesized from inexpensive raw materials (CO2 and propylene oxide), by in-situ chain-transfer polymerization, as shown in figure 3. The surface energies of the PS block (42.4 mJ m⁻²) and the PPC block (42.9 mJ m⁻²) are almost equal at room temperature and remain quite close at temperatures below 200 °C, which enables easy formation of a perpendicular structure at the free surface. Different perpendicular morphologies (e.g. cylinder and lamellae) with sub-10 nm half-pitch size have been formed through thermal annealing. By applying the chemo-epitaxy method of DSA, 5× density multiplication was achieved with ordered features obtained over a long range on the substrate [16]. These experimental results indicate that PS-b-PPC is compatible with existing DSA processes, making it a promising candidate for sub-10 nm DSA.

2.1.1.3. Polystyrene-block-poly(lactic acid-alt-glycolic acid) (PS-b-PLGA). PS-b-PLGA is a new type of high χ BCPs synthesized by combining atom transfer radical polymerization and ring-opening polymerization. It has a high χ value (0.155 at 150 °C and 0.098 at 200 °C). By tuning the molecular weight of the blocks, L0 of PS-b-PLGA can be customized from 27 nm down to 13.5 nm. Similar to PS-b-PPC, the constituent blocks of PS-b-PLGA have similar surface energies (45.5 mJ m⁻² for PS block and 47.8 mJ m⁻² for PLGA), which makes forming a through-film perpendicular structure simple. Figure 4 describes a typical DSA process with PS-b-PLGA using the chemo-epitaxy method, in which L0 is the period of the guiding pattern, varying from 46 nm to 66 nm. Defect-free line patterns can be obtained by selecting the proper annealing temperature and period of guiding pattern (L0). So far, PS-b-PLGA has been demonstrated to form a perpendicular lamellar morphology on guiding stripes to achieve density multiplication, making PS-b-PLGA another potential candidate for sub-10 nm DSA [31].

2.1.1.4. Polystyrene-block-poly(2,2,2-trifluoroethyl acrylate)s (PS-b-PTEFAs). PS-b-PTEFAs are fluorine-containing high χ BCPs synthesized by high-conversion transesterification of acrylate units of PS-b-PtBAs with the specific catalyst polyphosphoric acid. The χ value of PS-b-PTEFAs is >0.16 and the minimum achievable pitch size of PS-b-PTEFAs is around 10 nm for a lamellar structure. Like the other fully organic high χ BCPs mentioned earlier, PS-b-PTEFAs can be thermally annealed to form lamellar structures oriented perpendicular to the substrate (figure 5) [32].

2.1.1.5. Poly(5-vinyl-1,3-benzodioxole)-block-poly(pentamethyldisilystyrene) (PVBD-b-PDSS). PVBD-b-PDSS is another type of high χ BCP that was presented by Willson’s group. They demonstrated DSA of PVBD-b-PDSS via thermal annealing on guidelines formed by nanoimprint lithography. Their work focused on exploring the optimal process conditions for DSA of PVBD-b-PDSS, including guideline preparation, brush processing, film thickness, application of a top-coat, and pattern transfer (figure 6). A lamellar structure with 5 nm half-pitch size was achieved by DSA with density multiplication. The study revealed more process related details that will help improve the quality of the DSA process [33].

2.1.1.6. Poly(styrene-block-methyl acrylate) (PS-b-PMA). PS-b-PMA is a methyl acrylate based BCP that has a structure similar to PMMA. PS-b-PMA and PS-b-PMMA are similar in many aspects, such as equal etch resistance under O2 plasma, similar chemical properties under sequential infiltration synthesis (SIS) process, and near equal surface energies of the two constituent blocks. However, the most significant difference between these two BCPs is that the χ value of PS-b-PMA is much higher (~0.068 at 150 °C) than that of PS-b-PMMA (~0.039 at 150 °C), and the L0 of PS-b-PMA after microphase separation can be as low as 14 nm [34]. PS-b-PMA possesses all the merits of PS-b-PMMA but has a significantly larger χ value, which positively contributes to the efforts for developing new processing methods, and therefore, has great potential for sub-10 nm high-resolution patterning.

2.1.2. High χ BCPs with inorganic blocks. High χ BCPs with inorganic blocks, such as polyhedral oligomeric silsesquioxane (POSS), polyferrocenylsilane (PFS), polytrimethylsilylstyrene (PTMSS), and polydimethylsiloxane (PDMS), are potential candidates for sub-10 nm patterning. The incorporation of inorganic blocks increases the dissimilarity between the two blocks of the BCP, raising their segregation strength (χN). Additionally, the inorganic block in BCPs can be oxidized during reactive ion etching (RIE) and exhibits high etch resistivity, in some cases, serving as a hard mask for pattern transfer without additional processing steps. One of the most intensively studied categories of organic-inorganic BCP is BCPs containing PDMS. Ross and coworkers reported using PS-b-PDMS (χ = 0.27 at room temperature) to form cylindrical and lamellar structures with a half-pitch size (1/2 L0) of 10 nm [35, 36]. The same group also reported the assembly of poly(2-vinylpyridine)-block-poly(dimethyl siloxane) (P2VP-b-PDMS) whose χ value was a few times larger
Figure 2. Self-assembly of PS-\(b\)-PTMC BCP. (a) Height image of PS-\(b\)-PTMC BCP, \(V_{PTMC} \sim 0.47\), (b) height image of the BCP after fractionation, \(V_{PTMC} \sim 0.36\) and (c) phase image of self-assembled BCP. Reproduced from [30] with permission of The Royal Society of Chemistry.

Figure 3. (a) SEM image of a 17 nm SC (15.6, 0.47) thin film on silicon wafer coated with PS-r-PMMA brushes with \(F_{St} = 12\%\) via thermal annealing at 145 °C for 30 min; (b) GISAXS pattern; (c) \(q_z\) line cut at \(q_z = 0.0165\ \AA^{-1}\) of the same film at an incident angle of 0.2°. Reprinted with permission from [16]. Copyright (2019) American Chemical Society.

Figure 4. (a) Schematic illustration of the procedure used to create asymmetric chemical patterns and DSA of lamellae-forming PS-\(b\)-PLGA with 2× density multiplication under thermal annealing. (b) Top-down SEM images of SLG (9.5−13.2) films (30 nm in thickness) assembled on chemical patterns with \(L_L = 46−66\) nm under 160 °C, 180 °C, and 200 °C annealing. Reprinted with permission from [31]. Copyright (2018) American Chemical Society.
Figure 5. (a), (b) SFM phase images of PS-b-PTFEA32 film supported on a standard Si wafer. (a) The film was thermally annealed at 150 °C under vacuum for 12 h. (b) As-spun film. Chemical structure of P4TFMS is described with the schematic film preparation. (c)–(f) SFM phase images and corresponding 2D GISAXS patterns for (c) PS-b-PTFEA12.6, (d) PS-b-PTFEA23, (e) PS-b-PTFEA32, and (f) PS-b-PTFEA47 films supported on a P4TFMS mat. (g) $L_0$ of PS-b-PTFEA films to compare with that of the bulk BCPs. Reprinted with permission from [32]. Copyright (2018) American Chemical Society.

Figure 6. Images of nanoimprint lithography (NIL) guidelines (top), BCP directed self-assembly (middle), and cross-sectional STEM in conjunction with EELS mapping (bottom) for three surfaces investigated in this study: (a) SiO$_2$ with brush, (b) untreated SiO$_2$, and (c) thin Cr$_x$O$_y$ (2 nm) on SiO$_2$. The height of the NIL lines for the samples made on SiO$_2$ and Cr$_x$O$_y$ were approximately 12 nm and 8 nm, respectively. BCPs on SiO$_2$ were etched before STEM analysis, while the sample assembled on Cr$_x$O$_y$ was not. The starting BCP film thickness for all three samples was approximately 33 nm. The samples on SiO$_2$ were annealed at 190 °C for 2 min, while the sample prepared on Cr$_x$O$_y$ was annealed at 205 °C for 10 min. The scale bar for the top-down SEM images is 100 nm, and the scale bar for the cross-section EELS images is 15 nm. Reprinted with permission from [33]. Copyright (2017) American Chemical Society.

than PS-b-PDMS [37]. This polymer, assembled by solvent annealing, formed different morphologies (e.g. spheres, cylinders, hexagonally perforated lamellae, and lamellae) with a half-pitch size varying from 6 nm to 31 nm. More recently, Azuma et al synthesized a new BCP, poly(3-hydroxystyrene)-block-polydimethylsiloxane (P3HS-b-PDMS), with an estimated $\chi$ value as large as 0.39 at 150 °C. P3HS-b-PDMS was demonstrated to form lamellae and hexagonally packed cylinders with feature sizes ranging from 7.4 nm to 17.7 nm [38]. SVA was usually chosen for the high $\chi$ BCPs mentioned above for the sake of morphology and orientation control.

Wilson’s group synthesized several high $\chi$ BCPs, such as polytrimethylsilystyrene-block-poly(D,L-lactide) (PTMSS-b-PLA) and poly(styrene-block-trimethylsilylstyrene) (PS-b-PTMSS). Chemo-epitaxy and grapho-epitaxy methods were applied on PS-b-PTMSS to achieve a high density multiplication ($7 \times$) with a top coat layer to ensure perpendicular orientation of the lamellae structure [39]. Recently, Nakatani
et al developed a novel silicon-containing BCP, poly(POSS methacrylate-block-poly(2,2,2-trifluoroethyl methacrylate) (PMAPOSS-b-PTFEMA), with an interfacial affinity control unit to modulate the surface energy difference between the organic and inorganic blocks [40]. In this case, a vertically orientated lamellar structure formed through direct thermal annealing, without the application of an additional top-coat layer. The effective $\chi$ value of PMAPOSS-b-PTFEMA was estimated to be 0.45. DSA via graphoepitaxy formed a perpendicular lamellae structure with a half-pitch size of 8 nm, which indicates that PMAPOSS-b-PTFEMA is highly compatible with current DSA techniques. This work demonstrated the possibility of incorporating inorganic blocks in a BCP without adding complexity to the process flow.

In summary, the section above lists a few types of high $\chi$ BCPs. Regardless of its type, a high $\chi$ BCP need to meet several prerequisites to be a candidate for next generation DSA technology. These requirements include a high etch contrast between the constituent blocks and the ability to form a perpendicular morphology for patterning. Table 1 summarizes the basic properties of the high $\chi$ BCPs introduced in this section. Most of these high $\chi$ BCPs meet the necessary requirements. However, more efforts are needed to explore the optimal process conditions during the DSA formation process and the subsequent etching and pattern transfer processes. It is also necessary to study defect formation and prevention.

2.2. SVA for high $\chi$ BCPs

Incorporating high $\chi$ BCPs in next generation DSA requires new processing methods to replace the traditional thermal annealing step. The incompatibility between blocks of copolymer that creates a high $\chi$ value also limits the copolymer’s ability to self-assemble and form through-film structures [41]. Increasing the annealing temperature theoretically accelerates the self-assembly process, but several high $\chi$ BCPs have a low tolerance to high temperature. SVA—a process in which solvent vapor is used to control unit to modulate the surface energy difference between the organic and inorganic blocks [40]. During the SVA process, the solvent vapor pressure inside the sealed chamber is much lower than the pressure in the annealing chamber, leading to a different morphology from that of the bulk BCP. A neutral solvent uniformly swells the whole BCP, leading to a different morphology from that of the bulk BCP. A neutral solvent uniformly swells the whole BCP, preserving the original morphology. The solvent vapor pressure in the annealing chamber affects the actual pitch size and quality of the obtained BCP films. In general, sub-10 nm feature sizes can be achieved on a variety of high $\chi$ BCPs with SVA-based self-assembly. For example, Ross et al demonstrated that a cylindrical morphology of polystyrene-block-polydimethylsiloxane (PS-b-PDMS) with an 18 nm pitch ($L_0$) could be obtained using acetone-based SVA [45]. Park et al reported that solvent annealed polystyrene-block-poly(ethylene oxide) (PS-b-PEO) formed arrays of ordered cylinders with diameters as small as 3 nm [46]. Tada et al showed a morphological transition from cylindrical to spherical by SVA in CS$_2$ of a BCP composed of a poly(methyl methacrylate) block and a methacrylate-based block that contained polyhedral oligomeric silsesquioxane (PMMA-b-PMAPOSS) (figure 8) [47].

By choosing different solvents, different morphologies can be obtained from the same BCPs. For instance, Bosworth et al reported that SVA of poly (o-methylstyrene)-block-poly(4-hydroxystyrene) (PoMS-b-PHOST) with tetrahydrofuran
Table 1. Summary of various high χ BCPs and their properties.

| Block copolymers | χ (150 °C) | Half-pitch size | Processing methods | Reference |
|------------------|------------|-----------------|--------------------|-----------|
| Polystyrene-block-poly(methyl methacrylate) (PS-b-PMMA) | 0.039 | 11 nm | Thermal annealing/solvent vapor annealing Dry etching Good etch contrast | [25] |
| Polystyrene-block-poly(trimethylene carbonate) (PS-b-PTMC) | >0.039 | 8.5 nm | Thermal annealing | [28–30] |
| Polystyrene-block-poly(propylene carbonate) (PS-b-PPC) | 0.079 | 6–7 nm | Thermal annealing Low etch contrast | [16] |
| Polystyrene-block-poly(lactic acid-alt-glycolic acid) (PS-b-PLGA) | 0.155 | 7–14 nm | Thermal annealing | [31] |
| Polystyrene-block-poly(2,2,2-trifluoroethyl acrylate)s (PS-b-PTFEAs) | >0.16 | 5 nm | Thermal annealing | [32] |
| Poly(5-vinyl-1,3-benzodioxole)-block-poly(methylsiloxane) (PVBD-b-PDSS) | Unknown | 5 nm | Thermal annealing | [33] |
| Polystyrene-block-poly(methyl acrylate) (PS-b-PMA) | 0.068 | 7 nm | Thermal annealing Dry etching Good etch contrast | [34] |
| Polystyrene-block-polydimethylsiloxane (PS-b-PDMS) | 0.27 | 10 nm | Solvent annealing Dry etching High etch contrast | [35–37] |
| Poly(3-hydroxystyrene)-block-polydimethylsiloxane (P3HS-b-PDMS) | 0.39 | 7.4 nm | Solvent annealing Dry etching High etch contrast | [38] |

Figure 7. Schematic of the flow chamber for solvent annealing. Nitrogen acts as a carrier gas through an acetone solvent bubbler. Pure nitrogen is fed through a second line for dilution to lower the solvent activity. The flow chamber is equipped with a spectral reflectometer (Filmetrics, F-20 UV) to monitor the thickness change of the thin polymer film upon exposure to acetone vapor. Reprinted with permission from [15]. Copyright (2016) American Chemical Society.

(THF) vapor formed parallel cylinders, while hexagonally packed spheres were obtained from SVA of PoMS-b-PHOST with acetone [48]. In another example reported by Jeong et al., poly(2-vinylpyridine)-block-poly(dimethylsiloxane) (P2VP-b-PDMS) underwent SVA with a variety of solvents (e.g. isopropyl alcohol, ethanol, methanol, pentanol, acetic acid, and pyridine) to form several different morphologies (e.g. spherical, cylindrical, perforated lamellar, and lamellar)
Besides these examples, morphology can also be controlled by using a mixture of different solvents and tuning the volume ratios of these solvents in the mixture. For example, Chavis et al. used a mixture of methanol (MeOH) and THF to anneal poly(2-hydroxyethyl methacrylate)-block-poly(methyl methacrylate) (PHEMA-b-PMMA) [49]. Different morphologies, such as spherical, lamellar, cylindrical, and gyroid, were obtained by varying the volume/volume ratios of MeOH and THF. The morphology tuning capability of SVA expands the use of BCPs without changing the volume ratio \( f \) of the blocks in a BCP, thereby, reducing the need to synthesize a number of BCPs with different \( f \) values.

2.2.2. Orientation control using SVA. For high \( \chi \) BCPs to be used in lithography, it is critical that the BCPs can form long range-ordered, defect-free, vertically orientated structures. When applying SVA, perpendicularly orientation of lamellar or cylindrical structures is highly desirable, whereas transitions in morphology are undesirable. As discussed above, the selectivity of solvent in the SVA process determines the amount of morphological transition. For lithographical applications, a neutral solvent is a better choice for SVA. Another concern is that BCPs undergoing SVA must retain their ability to follow the guide patterns generated by chemoscriptaxy, a highly reliable and process friendly method in the PS-b-PMMA system. Research regarding SVA of high \( \chi \) BCPs on chemically patterned guide substrates is still emerging.

Russell’s group used acetone as a neutral solvent for SVA of P2VP-b-PS-b-P2VP to obtain a perpendicularly oriented lamellar structure on a patterned substrate with sub-15 nm features [50]. Xiong et al. conducted a more detailed study of DSA of P2VP-b-PS-b-P2VP on a chemically patterned substrate. In this work, the SVA step was integrated with DSA on a chemical pattern that was formed with independent control of its chemistries, line width (\( W \)), and period (\( L_s \)), as shown in figure 9. The concentration of acetone was controlled by adjusting the flow rates of the carrier gas (\( N_2 \)) and the diluting gas (\( N_2 \)). The experiments explored the influence of different process parameters, such as polymer composition, solvent volume fraction in solvated BCPs, \( W \) and \( L_s \) of the guiding patterns, and the composition of random copolymer brush in the chemical pattern between the guiding lines. The performance of two versions of PS-b-P2VP, diblock (PS-b-P2VP) and triblock (P2VP-b-PS-b-P2VP) over a range of solvent volume fraction (\( \phi_s = 0.2–0.31 \)) were compared. It was found that P2VP-b-PS-b-P2VP formed a clear lamellar structure with long correlation lengths when \( \phi_s \) increased from 0.2 to 0.31. However, the diblock PS-b-P2VP did not form a lamellar structure over the range of \( \phi_s \) values in their study. The observed difference in the solvent processing window was attributed to the difference between the \( \Phi_{ODT} \) (the polymer fraction at the order-disorder transition (ODT)) of the diblock and triblock of PS-b-P2VP. \( \Phi_{ODT} \) can be estimated from the effective \( \chi \) value (\( \chi_{eff} \)) in the solvated BCP system (\( \chi_{eff} = \chi\Phi^\alpha \)), where \( \alpha \) is determined by \( L_0 \) in the solvent. The calculated \( \Phi_{ODT} \) values were 0.45 and 0.53 for P2VP-b-PS-b-P2VP and diblock PS-b-P2VP, respectively, indicating that diblock PS-b-P2VP is closer to the ODT than P2VP-b-PS-b-P2VP. In other words, compared with diblock PS-b-P2VP, P2VP-b-PS-b-P2VP can tolerate more solvent while maintaining microphase separation.

The effects of chemical patterns on the integrated process were studied in another set of experiments. DSA of P2VP-b-PS-b-P2VP using acetone annealing (\( \phi_s = 0.26 \)) was performed on chemical patterns with \( W \) ranging from 0.92\( L_0 \) to 1.66\( L_0 \). The best perpendicularly lamellar structures were obtained at \( W = 1.0 \) \( L_0 \) and 1.5 \( L_0 \) (figure 10). P2VP-b-PS-b-P2VP using SVA with acetone (\( \phi_s = 0.26 \)) effectively compensated for differences in \( L_s \) of the chemical patterns, both at 3\( \times \) and 4\( \times \) density multiplication (figure 11). When
examining the influence of chemical brush composition, it was found that P2VP-b-PS-b-P2VP can form desired vertical lamellar structure with a styrene fraction in a poly(styrene-random-2-vinylpyridine) random copolymer (P(S-r-2VP)) ranging between 50% and 75% [15]. These comprehensive studies provide a deeper understanding of the SVA process and its compatibility with existing DSA techniques, broadening the range of high $\chi$ BCP candidates for DSA in advanced lithography.

### 2.2.3. Solvent-polymer interaction in the SVA process

The use of neutral solvents on high $\chi$ BCPs during annealing has the advantage of retaining the original domain structure. In the previous example, acetone was chosen as the neutral solvent for P2VP-b-PS-b-P2VP. According to the work of Wan et al., acetone was selected for several reasons, including its wide process window, compatibility with the chemical pattern of DSA, and quick evaporation during the drying step. In most cases, it is assumed that the solvent distribution inside the BCPs is uniform. However, the role that solvent distribution in BCPs plays in the SVA process has not been clearly explained. The work reported by Xiong et al. aimed at exploring the solvent distribution effect on BCPs during SVA process, comparing the effects of two neutral solvents, methyl ethyl ketone (MEK) and acetone, on P2VP-b-PS-b-P2VP [51]. MEK and acetone were used to anneal P2VP-b-PS-b-P2VP at different swelling ratios, ranging from 20% to 40%. When annealing with acetone, a perpendicular lamellar structure could be obtained at all of the examined swelling ratios. MEK, on the other hand, could not induce P2VP-b-PS-b-P2VP to form a fully ordered morphology at the 20% swelling ratio, as shown in figure 12. However, acetone accumulated at the domain interface during SVA, which resulted in smaller periods and larger grain sizes in the obtained lamellar structure. In contrast, the interaction between MEK and the BCP was weaker, leading to a smaller screening effect and a more uniform solvent distribution in the solvated BCP. Thus, the BCP in the MEK-solvated film had a larger effective $\chi$ value than the acetone-solvated film. Furthermore, it was also demonstrated that with MEK-based SVA, DSA of P2VP-b-PS-b-P2VP on a chemical guide pattern ($L_s = 100$ nm) could be performed to obtain lamellae with a pitch of 16.7 nm (figure 13). This work provides possible ways to determine the quality of a solvent in the SVA process, which is valuable for future research on SVA with other high $\chi$ BCPs.

### 2.3. Top-coat layer for thermal annealing

For high $\chi$ BCPs with blocks that have dissimilar surface energies, thermal annealing causes the block with lower

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**Figure 9.** Complete DSA and etching process, including generation of a chemical pattern with period ($L_s$) and line width ($W$) from a film of cross-linked polystyrene brush (XPS), spin coating and solvent annealing a block copolymer film on the chemical pattern, sequential infiltration synthesis of AlO$_x$ in one block of the assembled copolymer, and selective polymer removal and etching of the underlying silicon substrate. Reprinted with permission from [15]. Copyright (2016) American Chemical Society.
surface energy to form a uniform domain at the free surface. Applying a top-coat layer on a thin film of BCPs is an effective method of mitigating the surface energy differences and thereby enabling the formation of through-film perpendicular domain structures with thermal annealing [52]. There are several basic requirements for a top-coat beyond mitigating surface energy differences. An effective top-coat should be chemically stable and non-reactive with the underlying BCPs. The deposition process for the top-coat layer should be compatible with the existing fabrication process. After
Figure 11. Effect of varying chemical pattern period $L_S$ on the directed self-assembly of P2VP-$b$-PS-$b$-P2VP with $3 \times$ and $4 \times$ density multiplication and solvent vapor annealing in acetone on the chemical patterns. The top-down SEM images of the assembled triblock copolymers were taken immediately after block-selective infiltration of AlO$_x$. The scale bar in each table applies to all the SEMs in the table. The right column of each table contains the power spectra density corresponding to each SEM image. The power spectra were used to determine the pitch of the assembled block copolymer, $L_p$, shown next to the peak in each power spectrum. The vertical dashed line in the power spectra corresponds to $L_{0.26} = 16.3$ nm. Reprinted with permission from [15]. Copyright (2016) American Chemical Society.

self-assembly of the BCPs, the top-coat layer should either be easily removable or penetrable to the materials in subsequent deposition steps.

There are different ways of applying a top-coat layer on a film of BCPs. Spin coating is the most commonly used method. For a spin-coated top-coat, potential problems include the polarity of the top-coat polymer and the absorption of the top-coat solvent by the BCP. These problems can be overcome by employing a polarity switching top-coat, as reported by Willson et al [53]. The top-coat polymer was first dissolved in an aqueous solution and then spin-coated onto the BCP. Upon baking, the top-coat transformed into a less polar state and neutralized the top interface. A top-coat layer can also be applied via vapor deposition. For instance, Suh et al demonstrated a vapor-phase deposited top-coat on poly(2-vinylpyridine)-block-polystyrene-block-poly(2-vinylpyridine) (P2VP-$b$-PS-$b$-P2VP (VSV)) to realize sub-10 nm patterning [54]. The top-coat was deposited by initiated chemical vapor deposition (iCVD) with a controlled film thickness of several nanometers, as shown in figure 14. This method eliminates the solvent and allows for better control of film quality. The thin top-coat, without being removed, was easily penetrated in a subsequent pattern transfer step based on atomic layer deposition (ALD), indicating its potential to be applied on a variety of high $\chi$ BCPs.
2.4. Other annealing technologies

Besides thermal annealing and SVA, other techniques for BCP processing techniques have emerged, such as laser annealing and microwave assisted annealing. For example, Ober et al. used a laser spike to anneal a silicon-containing BCP, polystyrene-block-polydimethylsiloxane (PS-b-PDMS), to obtain vertically orientated cylinders. The laser spike method significantly shortened the annealing time to several milliseconds [55]. Morris’ group used microwave heating for BCP annealing and initiating microphase separation [56]. Ross et al. used a combination of different technologies, such as solvent annealing with electron irradiation to treat high $\chi$ BCPs [57]. The successful application of these techniques requires detailed studies of various process parameters, such as BCP film thickness, and processing energy, time and temperature. More efforts are needed to identify the optimal process conditions and the compatibility of these techniques with BCPs under different processing requirements.

2.5. Simulation on the thermodynamics of the DSA of BCPs

Considering that BCPs are composed of high molecular weight molecules, it is more cost-effective to simulate the equilibrium thin film morphologies and the assembly kinetics using a coarse-grained model. Each monomer constituting the polymer can be represented by a single unit, without sacrificing the free energy expression of the BCP phase, and the quantitative description of the assembly’s thermodynamics. The formation of thin film morphology can be precisely predicted by assigning the surface tension and interacting parameters between each block and the top/bottom surface (most often consistent with the bulk values).
Figure 14. Schematic of the iCVD top-coat process. The vapor-phase monomer and initiator enter the chamber through different inlets and flow through the heated filaments. The initiators form radicals near the heated filaments. Then, the monomers and radicals adsorb on the cooled free surface of the BCP film and partially diffuse into the BCP film. Finally, a cross-linked top-coat film grows from the surface of the BCP film via free-radical polymerization.

DSA usually requires a guide patterns to direct BCPs into desired patterns (e.g., lines, circles). The guide pattern’s quality and properties are crucial to the defect-free assembly and complete registration to the designated position. However, experimenting with different sets of annealing of samples to identify the influence of various geometrical, chemical, or thermal processing parameters is time-consuming. While using the coarse-grained model to simulate the thermodynamics based on the self-consistent mean field (SCMF) theory [58], starting from a random configuration, a Flory-type monomer-monomer interaction is adopted, and the evolution of free energy in the many body system is minimized. These simulations utilize different algorithms to provide physical insights about the assembly process of BCPs, which is extremely helpful for determining the processing window of the guide patterns and the potential causes of defects in assembled BCPs. For example, Li et al. employed single-chain-in-mean-field simulations to study the motions of dislocations in symmetric diblock copolymers. The interaction forces and free energies involved in dislocation formation have been thoroughly studied. They also figured out an intermediate segregation condition to annihilate dislocation defects [59]. In the work of de Pablo et al., new optimization algorithms based on evolutionary computation were used to simulate the DSA process of triblock BCPs. The width and period of the guide chemical pattern were optimized to obtain a defect-free lamellar nanostructure [60]. The same group also presented Monte Carlo simulation work on acquiring the optimal geometry and chemistry of the chemical guiding pattern for PS-b-PMMA [61]. In addition to their thermal annealing model, Hur et al. developed the solvent absorption and evaporation model, which simulates the solvent assisted directed-assembly of BCP thin films [62]. The effect of solvent distribution to the assembly kinetics and the solvent removal rate to the defect reduction have been intensively studied [51]. In these works, the simulation results agreed with the experimental results, promising great potential for the understanding of the DSA process, as well as the tracking and analysis of assembly defects.

3. Pattern transfer techniques

In DSA lithography, a BCP undergoes microphase separation to form specific morphologies that are useful for patterning. One of the critical steps in DSA lithography is effectively transferring the assembled nanostructure to the underlying substrate with high fidelity. The pattern transfer step is usually accomplished by selectively removing the microdomains from one of the blocks in the BCP so that the remaining structure can act as an etch mask, similar to the function of photore sist. Different techniques have been developed to produce a BCP etch mask, such as dry and wet etching, block-selective infiltration of inorganic materials, and incorporation of a lift-off process. For example, when PS-b-PMMA is immersed in acetic acid, the PMMA block dissolves and the PS structure remains as etching mask. O₂ RIE can also be used to selectively remove PMMA in PS-b-PMMA, but the etch contrast between the PS and PMMA blocks is very low (~1:2.5 in case of O₂ plasma treatment). SIS of inorganic materials into the PMMA domains significantly enhances the PMMA block’s etch resistance and increases the etch contrast between the PS and PMMA domains. Another method of overcoming the low etch contrast of PS-b-PMMA is to deposit a thin layer of metal and use a lift-off process to remove the PMMA microdomains, yielding a metal hard mask that can be used for pattern transfer [63–65].

As DSA lithography is enhanced to the sub-10 nm level, new challenges for pattern transfer from high χ BCPs arise, such as the difficulty in etching narrower lines and maintaining line width uniformity over a long-range. Increasing the etch
contrast between a BCP’s blocks enhances the overall quality of the resulting nanostructure. This chapter covers the most common methods for pattern transfer with high $\chi$ BCPs. Previous research on other methods using metal deposition and lift-off processes are also presented. Depending on the properties of high $\chi$ BCPs, different methods can be employed to accomplish the pattern transfer process. RIE can be applied directly to high $\chi$ BCPs that contain inorganic blocks, given the inherent high etch contrast between its two blocks. SIS can be applied to enhance the etch contrast in a variety of fully organic high $\chi$ BCPs.

3.1. Direct RIE

RIE is a manufacturing process that is widely used in in the semiconductor industry. It is considered the optimal method for BCP pattern transfer. RIE is cleaner and more efficient than wet etching, which may affect the BCP’s structure and chemical stability due to solvent residue. During RIE, the ionized etchant gas removes a specific polymer through a chemical reaction to form volatile products, or through a physical sputtering process [66]. Using RIE to selectively remove the domains of one block in a BCP requires a high etch contrast between the BCP’s constituent blocks. As previously mentioned, PS-$b$-PMMA can be etched by RIE, but with a low etch contrast ($\sim$1:2.5 in case of O$_2$ plasma treatment), and the remaining PS mask is inadequate for the further pattern transfer to the underlying substrate. Organic-inorganic high $\chi$ BCPs naturally have a high etch contrast because the constituent blocks react differently with the etchant gas during RIE. Usually, the inorganic block reacts with the etchant gas (i.e. O$_2$) to form a nonvolatile inorganic product (e.g. metal oxide), turning the inorganic block into a hard mask for further pattern transfer to the underlying substrate, while the organic block volatilizes through chemical reaction and sputtering. Several studies indicate that RIE is effective for patterning organic-inorganic BCPs. For example, in Ross’s group, Jung et al used RIE to etch away the PS in cylinder-forming PS-$b$-PDMS. The ionized O$_2$ gas reacted with the silicon in PDMS, forming oxygen-plasma-modified PDMS in the PDMS microdomains. After PS removal, further pattern transfer can be done from the SiO$_2$ hard mask to the underlying silicon substrate using RIE, as shown in figure 15 [67]. Aissou et al reported direct RIE patterning of another silicon-containing BCP, semicrystalline poly(1,1-dimethyl silacyclobutane)-block-poly(methyl methacrylate) (PDMSB-$b$-PMMA). During RIE, the PDMSB block can be turned into a SiC hard mask while PMMA can be easily removed. PDMSB-$b$-PMMA exhibits an etch contrast of 15:1 in RIE [68, 69]. Lammertink et al conducted a detailed study on direct RIE etching of a BCP that contained poly(ferrocenyldimethylsilane) (PFS), an inorganic polymer containing Fe and Si elements. Varying the RIE process parameters (e.g. power) increased the etch contrast between PFS and the organic block from 1:20 to 1:50 [70].

Even though pattern transfer with organic-inorganic BCPs can be realized in a very simple way, the incorporation of inorganic elements (e.g. metal ions) may cause other problems, such as metal ion contamination or difficulty eliminating the inorganic hard mask after pattern transfer. For example, Fe is a notorious contaminant in IC devices. Separately, the removal of SiOx requires the use of HF, a hazardous acid which requires special handling. The process parameters during RIE, such as etching power and duration, significantly affect the line width of the obtained hard mask and need to be studied and optimized for high fidelity pattern transfer.

Researchers have also explored the possibility of using etchant gases other than O$_2$ in RIE. For example, N$_2$ RIE has been used to pattern a fully organic high $\chi$ BCP, polystyrene-block-poly(4-vinylpyridine) (PS-$b$-P4VP), that shows moderate selectivity towards the P4VP block (2.2:1) [71]. The etch contrast of PS-$b$-P4VP blocks under N$_2$ RIE is lower than other high $\chi$ organic-inorganic BCPs but is comparable to PS-$b$-PMMA under O$_2$ RIE. Direct RIE patterning of fully organic high $\chi$ BCPs remains challenging with difficulties in pattern preservation and defect prevention, especially for BCPs with film thicknesses suitable for sub-10 nm lithography.

3.2. Sequential infiltration synthesis

The SIS technique was first developed by Tseng et al in Argonne National Laboratory [72]. The driving force for developing SIS was to enhance the etch resistance of the organic block in BCPs. The SIS technique utilizes ALD to introduce inorganic reactants to a specific block in a BCP. Usually, one block in a BCP reacts with the ALD reactants and forms a metal oxide, while the other block is completely inert to these reactants and serves as a reaction stop. The chemical reaction only occurs within the reactive block. To date, successful deposition of a numerous of metal oxides, such as Al$_2$O$_3$, TiO$_2$, and ZnO, in a variety of BCPs has been demonstrated. For example, Darling’s group used trimethylaluminum (TMA) and H$_2$O to form Al$_2$O$_3$ in the PMMA block of PS-$b$-PMMA [72]. They also presented infiltration of PMMA block with other inorganic elements to form TiO$_2$, SiO$_2$, and ZnO [73]. The SIS technique can be extended to process other high $\chi$ BCPs. Xiong et al used SIS to deposit Al$_2$O$_3$ in P2VP lamellae in PS-$b$-P2VP as well as in P2VP-$b$-PS-$b$-P2VP triblock copolymer to realize high fidelity pattern transfer to the underlying silicon substrate. The resulting pattern of etched silicon is shown in figure 16 [15, 54]. They also reported the use of Al$_2$O$_3$-based SIS on a PS-$b$-PPC system to realize bit patterned media architecture [74]. Ishchenko et al applied TiO$_2$-based SIS on a cylindrical PS-$b$-P2VP system to form TiO$_2$ nanoarrays [75]. Their work demonstrated a complete process of BCP lithography, proving the feasibility of using high $\chi$ BCP lithography for sub-10 nm patterning.

Although SIS has proven to be highly effective for creating hard masks in BCPs, a thorough understanding of the SIS process, including the reaction mechanisms and the influence of process parameters during SIS, needs to be developed. Recently, researchers began exploring the mechanisms of SIS and the effects of process parameters during SIS. Argonne National laboratory conducted a series of detailed studies on the SIS process. In their studies of Al$_2$O$_3$-based SIS within PMMA, they determined that the reaction between the TMA
Figure 16. Sequential infiltration (SIS) enhanced pattern transfer onto an underlying silicon substrate. (a) Top-down SEM image of fingerprint lamellae after two cycles of SIS. (b) Top-down SEM after subsequent polymer removal using O₂ plasma etching. (c) Cross-sectional SEM image of the fingerprint lamellae after fluorine plasma etching to transfer pattern to Si, using AlOₓ as a mask (mask material removed by NaOH etching). (d) Top-down SEM image of registered lamellae after directed assembly on chemical pattern with pattern transfer to Si. Reprinted with permission from [15]. Copyright (2016) American Chemical Society.

precursor and PMMA is not a one-step process. Instead, an intermediate product quickly formed at an early stage and slowly converted into an Al-O covalent bond, as illustrated in figure 17. They also found that the purge time and reactant exposure time play crucial roles in the formation of the Al₂O₃ in PMMA (figure 18). The purge step is necessary to eliminate redundant reactions. However, a longer purge time negatively affects the reaction, resulting in less Al₂O₃ forming within the PMMA. In another study of TiO₂-based SIS within PMMA, they examined the reaction dynamics during SIS, including the effect of deposition cycles and reactant diffusion activity inside the PS-ₖ-PMMA structure. When the infiltration reaches saturation, applying more cycles of reactant does not result increase TiO₂ accumulation within the PMMA. Though the PS block is chemically nonreactive with the reactant, it serves as a diffusion path for the reactant to reach the available reaction sites in the PMMA [76, 77]. Lorenzoni et al performed another study on Al₂O₃-based SIS in PMMA to understand the morphology change of a BCP during SIS. They found that during SIS, PMMA expands in both horizontally and vertically, as shown in SEM images (figure 19). They also pointed out that a minimum of 5 ALD cycles is necessary for the formation of high-quality film and the optimal number of cycles ranges from 5 to 11 [78]. These studies
provide valuable insights into the exact chemistry during SIS and the mechanical properties of SIS-treated BCPs, which is extremely beneficial for the optimization of SIS recipes.

Recently, Frascatoli et al proposed using O$_3$ as a replacement for H$_2$O during Al$_2$O$_3$ SIS process in PMMA and proved there was no degradation in SIS performance. The SEM images shown in figure 20 provide a straightforward comparison between SIS with O$_3$ and H$_2$O. Both strategies show excellent pattern quality. Using O$_3$ as a precursor has several advantages, such as higher reactivity, reducing purge time, and obtaining a pattern with high aspect ratio (greater than one) [79].

In summary, the SIS technique significantly enhances the processability of fully organic high $\chi$ BCPs. The resulting metal oxide hard mask (e.g. Al$_2$O$_3$) possesses a higher etch resistance than that of SiO$_x$. These metal oxide hard masks can be easily developed by KOH, without involving hazardous chemicals.

3.3. Lift-off process

In sections 3.1 and 3.2, we discussed forming etch masks on BCPs through direct dry etching and SIS. In addition to these two methods, a metal lift-off process can also be applied to BCPs to realize pattern transfer. This process includes removing one phase in BCPs to generate a porous template, depositing a thin layer of metal on the porous BCP template, and eliminating the remaining BCP to obtain a metal nanostructure. In some cases, the obtained metal nanostructure after lift-off can be used as a hard mask for substrate etching. There are several reports using metal hard masks for pattern transfer. Russell’s group used a sphere-forming PS-b-PDMS as a template for chromium deposition. After lift-off of the remaining PDMS polymer, a chromium mask was created for patterning the silicon substrate [80].

One recent work from Willson’s group demonstrated pattern transfer to the underlying SOC film with a chromium hard mask created from a poly(5-vinyl-1,3-benzodioxole-block-pentamethyleneisilylstyrene) (PVBD-b-PDSS) template through a lift-off process [33]. Tu et al also summarized different ways of making a Co nanostructure (e.g. lines and dots) on a PS-b-PDMS template. The methods included a damascene process and a lift-off process with a sacrificial PMMA layer [69]. Although a metal hard mask exhibits higher etch resistance, resulting in a more robust pattern transfer process, processing this metal layer requires additional treatment (e.g. UV or ozone) of BCPs and the use of organic solvents during the lift-off step, making this method less reliable and efficient compared with direct RIE and SIS.

A more attractive application of the lift-off method is the fabrication of nanodot and nanowire arrays on a BCP-coated substrate. In this case, the deposited nanostructure serves as a functional layer rather than a hard mask. For instance, Hong et al employed a PS-b-PMMA lift-off process to fabricate high-density Cr nanodot arrays and successfully implemented a memory device on this Cr dot array structure [81]. Ross’s group used a PS-b-PDMS template to produce a variety of sub-10 nm metal nanowires, such as Ti, Pt, Co, Ni, and Au [69, 82]. Kim et al fabricated gold nanowire arrays inside a micropattern by combining photolithography and BCP lift-off processes [83]. Huang et al used a PS-b-PMAA template to grow InAs nanowires, as shown in figure 21 [84]. Apart from metal nanostructures, this process can also be used for the fabrication of metal oxide nanowire arrays in other applications.

In short, fabrication of metal/metal oxide nanostructures in the sub-10 nm field is of great importance for the implementation of a variety of functional devices, like memory chips and transistors. BCP lithography has shown great potential to achieve mass production of these nanostructure arrays. However, current methods for fabricating BCP templates require further improvement with process-friendly techniques.

4. Industrialization of DSA technology

Academically, advancement of DSA technology is continuing with many successes, especially in the field of sub-10 nm patterning. A vast number of high $\chi$ BCPs have been developed along with new processing methodologies [31, 32, 85–87]. These research works focus on the synthesis of high $\chi$ BCPs, exploring the intrinsic properties of the BCPs and introducing new chemistry to induce self-assembly of BCPs. Beyond academic research, there is significant interest in bringing DSA technology into semiconductor manufacturing because of its potential for producing high-quality sub-10 nm patterning when combined with other lithography techniques, such as immersion lithography and EUV. Additionally, the DSA technology simplifies the manufacturing process compared with multi-patterning techniques and may lower the cost of device fabrication. Implementing DSA technology in industry requires a comprehensive understanding of the compatibility of DSA procedures, materials, and process conditions with the existing semiconductor manufacturing line. Even if the BCPs of interest can be mass-produced, their long-term stability may still be a problem due to the materials used in DSA. Also, processing BCPs involves solvents that are rarely used for semiconductor fabrication, and therefore, may lead to compatibility problems. In terms of the process, it is necessary to choose suitable facilities and optimize the processing conditions to achieve high throughput. Additionally, selecting effective tools for defect inspection is needed to discover material and process deficiencies. To achieve these goals, researchers from IMEC and their partners from universities and semiconductor companies practiced DSA technology on a 300 mm production line in a fab environment to study the influence of different processing conditions and to characterize defectivity levels in the process. They also investigated improvements in DSA that are necessary for its integration into industrial production. Experiments regarding different process flows (e.g. graphoepitaxy, chemo-epitaxy), choice of materials (e.g. solvent, brush composition), and defect inspection, identification, and prevention were carried out to address the most important aspects in DSA industrialization. This chapter reviews the complete process of DSA-based fabrication on a 300 mm wafer to understand the progress achieved and challenges ahead for DSA industrialization. The chapter concludes
Figure 17. Candidate structures for PMMA-TMA species. The lowest-energy configuration for two physisorbed structures \((O \cdots Al(CH_3)_3)\) where Al-CH\(_3\) group is interacting with (a) C = O and (b) C-O-R groups of PMMA, respectively. (c) The geometrically optimized covalent structure \((O-Al-(CH_3)_2)\), in which one of the TMA CH\(_3\) groups has been shifted to the C that was formerly part of the C = O group. Reprinted with permission from \([77]\). Copyright (2014) American Chemical Society.

Figure 18. FE-SEM images of 30 nm pitch PS-b-PMMA lamellae treated with one cycle of SIS and etched by an oxygen plasma. TMA was exposed for (a) 180 s and (b) 7200 s with 300 s purge time in both cases. With longer the amounts of deposited Al\(_2\)O\(_3\) increases with longer TMA exposure times. Reprinted with permission from \([77]\). Copyright (2014) American Chemical Society.

with a discussion of hole shrinking as a potential application for DSA technology.

4.1. DSA technology on a 300 mm track

The continuous development of DSA technology results in diverse process flows and processing conditions. However, not all of the process flows fit the stringent requirements of an industrial environment. Unlike in the laboratory, where DSA of BCPs can be easily realized on a relatively small sample substrate, implementing DSA of BCPs on a 300 mm wafer presents new challenges for achieving wafer-level film uniformity and low defectivity while maintaining a large process window. Careful analysis of each processing step is needed to improve the bottleneck step and determine the root causes of different defects.

IMEC designed a series of experiments targeting these problems. DSA of PS-b-PMMA was used in most of the studies, as PS-b-PMMA is one of the most extensively studied BCPs with well-known properties and processing conditions. Their examination of PS-b-PMMA-based DSA on a 300 mm track included selecting the best process flow, studying the influence of materials, and inspecting for defects.

4.1.1. Investigation of process flows. In the early stage of adopting DSA technology on 300 mm wafers, efforts were made to investigate mainstream process flows and determine the most suitable candidate. The process flows under investigation included DSA based on graphoepitaxy and chemoepitaxy. Somervell \textit{et al} from IMEC conducted a thorough study of three process flows on a 300 mm wafer: graphoepitaxy, lift-off chemo-epitaxy and trim-etched guide chemoepitaxy \([88]\). The process flow for graphoepitaxy is illustrated in figure 22. The patterned photoresist was used as the guide pattern to direct BCP self-assembly.

One major issue with the graphoepitaxy process flow is that the quality of the assembled BCP pattern, such as the line edge roughness, largely depended on the quality of the photoresist guide pattern, whose roughness is usually difficult to control. Moreover, to create an acceptable guide pattern, the exposure dose needed to be strictly controlled during lithography, resulting in a very small process window \((47–49 \text{ mJ cm}^{-2})\). Other issues included temperature stability of the selected photoresist guide pattern, and the waste of wafer space due to the placement of guide patterns. However, the waste of wafer space may be alleviated when the size of the guiding structure approaches the feature size, as demonstrated in the academic work of Bita \textit{et al} \([89]\).
**Figure 19.** (a) SEM top views of vertical lamellae in fingerprint orientation obtained with PS-b-PMMA. SIS-infiltrated lamellae tend to show a higher contrast: what appears dark in the left panel (PMMA plasma-removed domains) is instead brighter when imaging an infiltrated sample. Scale bar = 200 nm. (b), (c) AFM topography acquired in tapping mode of PS-b-PMMA samples with random lamellae in vertical configuration: (b) pristine and (c) treated with five SIS cycles. (d) Two height profiles confirming PMMA swelling due to SIS. Scale bar = 50 nm. (e)–(g) Topography, modulus map, and adhesion map, respectively, acquired in PeakForce tapping mode. As expected, the infiltrated PMMA phase (light green in the modulus map) shows the reverse contrast in the adhesion map. The color scales in (e) and (f) are nonlinear. All scale bars in (e)–(g) represent 200 nm. Reprinted with permission from [78]. Copyright (2017) American Chemical Society.

**Figure 20.** FE-SEM images of perpendicular PS-b-PMMA lamellae before infiltration (a), (f) and after infiltration (b)–(e) and (g)–(j). From (b)–(e) PS-b-PMMA lamellae infiltrated with an O\(_3\)-based SIS process, respectively, for 1, 3, 5, and 10 SIS cycles. From (g)–(j) PS-b-PMMA lamellae infiltrated with an H\(_2\)O-based SIS process for the same series of incremental SIS cycles. The square side corresponds to 500 nm. Reprinted with permission from [79]. Copyright (2017) American Chemical Society.
The second process studied was lift-off chemo-epitaxy flow, as shown in figure 23, in which a neutral layer was directly coated onto a photoresist pattern. After lift-off of the photoresist, the remaining neutral layer and the underlying anti-reflective coating served as the chemical guide pattern for BCP self-assembly. Compared with graphoepitaxy, lift-off chemo-epitaxy showed a much larger tolerance to dose variation during lithography-based guide pattern creation (13.5–17.5 mJ cm\(^{-2}\)). Unlike graphoepitaxy, this process flow was very sensitive to the thickness of the photoresist and the coated BCP. It was found that a thick (e.g. 90 nm) photoresist film may cause the guide pattern to collapse during lift-off. Additionally, the guide pattern lost the ability to direct the self-assembly of BCPs thicker than 40 nm. Thus, optimization of the film thickness of the photoresist and the BCPs is required to guarantee a successful DSA process. For this process, the
Figure 24. Schematic for trim-etched guide chemo-epitaxy process flow. Reproduced with permission from [88]. © (2012) Copyright Society of Photo-Optical Instrumentation Engineers (SPIE).

Figure 25. Evolution of defects in the DSA process. Reproduced with permission from [95]. © (2013) Copyright Society of Photo-Optical Instrumentation Engineers (SPIE).

Figure 26. Defect Pareto chart by best mode inspection. Reproduced with permission from [97]. © (2014) Copyright Society of Photo-Optical Instrumentation Engineers (SPIE).
effects of different density multiplications (e.g., 4× and 3×) were compared. Density multiplication (4×) achieved a suitable balance between different forces and demonstrated superior performance.

The last process examined was trim-etched guide chemo-epitaxy (figure 24). This process performed much better in both 4× and 3× density multiplication than the lift-off chemo-epitaxy process. When comparing these three process flows, it was observed that chemo-epitaxy out-performed graphene-epitaxy in terms of a larger process window (17 mJ cm⁻² to 25 mJ cm⁻²) and superior BCP pattern quality on the wafer.

In the case of chemo-epitaxy, lift-off chemo-epitaxy used the preferential silicon anti-reflective coating under the neutral layer to direct the self-assembly of the BCP. Trim-etch chemo-epitaxy utilized a guide pattern consisting of alternating neutral and preferential stripes to direct BCP self-assembly on a much more planar surface. Therefore, the trim-etch chemo-epitaxy process exerted fewer restrictions on the BCP film, which improved the BCP pattern quality. Trim-etched guide chemo-epitaxy was selected as the best potential process flow for DSA industrialization. The following sections present additional studies on process parameters and defect levels.

4.1.2. Defectivity study. As one of the potential patterning techniques within semiconductor industry, DSA needs to prove that it can achieve high pattern fidelity with low defectivity. The defectivity study in IMEC was carried out based on the trim-etched guide chemo-epitaxy flow on a 300 mm wafer [90–94]. In this study, primary attention was paid to the following aspects: defect inspection, defect cause analysis, and defect prevention. In an earlier work, Delgadillo et al used a broadband brightfield optical inspection system as the primary inspection tool for defect detection. In order to identify the source of defects and different defect types, inspection was performed at the end of each step in the chemo-epitaxy flow, including SiN deposition, crosslinkable polystyrene (X-PS) coating, resist exposure, resist trimming, neutral layer grafting
Figure 29. Fin formation using patterns from the PMMA-phase. (a) Process flow for forming groups of silicon on insulator (SOI) fins with a controlled fin spacing. A tone inversion operation is applied after etch transferring the DSA pattern into an organic planarizing layer (OPL). The tone inverted image is then transferred into a fin hard mask layer and 20 nm of SOI. (b) A top-down scanning electron microscope (SEM) image of a group of fins formed with the process shown in (a). The space between groups of fins is defined by the DSA guiding pattern. (c) A transmission electron microscope (TEM) image of 29 nm pitch SOI fins formed with the process shown in (a). Reprinted with permission from [108]. Copyright (2014) American Chemical Society.

and rinsing, and BCP processing (PMMA removal). The contribution of each step to the defect density is plotted in figure 25 [95]. It was observed that the defect density increased dramatically (~500 defects cm$^{-2}$) after the X-PS coating step. Both the neutral layer grafting and BCP coating steps generated significant amounts of defects. The most common defects in this process were white spots and particles, which led to dislocations. Interestingly, DSA of BCP may rectify a substantial number of defects attributed to the X-PS coating step. It is believed that dewetting of the X-PS material caused the white spots, and particles were introduced during the brush grafting step [22, 96]. In a subsequent study, Ito et al presented simulation and experimental results of a 10× enhancement of the signal-to-noise ratio in defect detection. Their findings suggest that defect inspection is most efficient when performed after the pattern transfer step. The types and morphologies of various defects are summarized in figure 26, among which dislocation, bridges, opens, and line bends were most frequently observed [97].

The IMEC’s initial study suggests that while the trim-etched guide chemo-epitaxy flow is highly adaptable to the 300 mm wafer manufacturing process, it demonstrated a defect level (~500 defects cm$^{-2}$) above the industrial standard. This high defect level was mostly associated with the materials instead of the process itself. Therefore, IMEC focused their efforts on defect reduction. A design of experiments (DoE) approach was adopted to analyze the relation between defect density and several vital process parameters, such as the exposure dose for the pre-pattern, BCP annealing time and temperature, and the etch depth during pattern transfer. The correlation between defect density and these variables is depicted in the plots in figure 27. In general, increases in exposure dose, annealing time, and annealing temperature had positive effects on defect reduction, while longer etch time increased the defect density. A more detailed analysis revealed that both dislocation and bridge defects were sensitive to the dimensions of the guide pattern. It was observed that a decrease in the dislocation defects was accompanied by an increase in bridge defects, which may imply a slight correlation between these two defects. The researchers speculated that the bridge defects may result from the healing of dislocation defects. Based on a series of DoE analyses, BCP and neutral layer composition as well as annealing time and temperature were co-optimized, unnecessary steps (e.g. soft bake) were removed to eliminate defects to a large extent. These actions initially reduced the defect density to 200 defects cm$^{-2}$ and ~24 defects cm$^{-2}$ by the end [98].

Overall, fitting DSA technology into the semiconductor manufacturing process and fulfilling the strict industrial requirement of low defect levels is a demanding process. As the pioneer in practicing DSA on 300 mm wafer production, IMEC has made significant progress in evaluating the DSA technology from material and process aspects. Provided that most of the defects are related to materials, the defect density can be effectively minimized. However, problems such as material maturity and some undetectable defects remain as obstacles for DSA commercialization.

4.2. DSA for hole shrinking

The increasing demand for patterning ever smaller contact holes (sub-30 nm) in IC manufacturing exerts enormous
pressure on traditional lithography and forces the semiconductor industry to seek better, and in some cases entirely new solutions. Common hole patterning techniques include ALD and double patterning. ALD can achieve high-resolution patterning, but the deposited metal oxide at the bottom of the hole is difficult to remove, which significantly affects the metallization step. Double patterning requires expensive masks and tedious patterning steps. As a high-resolution patterning technique, DSA cannot only realize line/space patterning, but also has immense potential in patterning a hole structure without using masks or removing any hard residues. The first attempt at using DSA for hole patterning was performed in a PS-b-PMMA system. Unlike line/space patterning, where the chemo-epitaxy flow is the preferred process based on experimental trials with 300 mm wafers, both grapho-epitaxy and chemo-epitaxy are usable for hole patterning applications [99–101]. Similar to line/space patterning, defectivity is of great importance in evaluating the feasibility of DSA for hole patterning. Possible improvement needs to be made to reduce defect density.

4.2.1. Hole shrinking based on different DSA processes. Applying the DSA technique to hole patterning has attracted lots of attention from semiconductor industry. Several leading research groups in the semiconductor industry have carried out experiments on DSA-based hole patterning on 300 mm wafers. The choice of process flows included both the grapho-epitaxy method and the chemo-epitaxy method and was based on lamellaeor cylinder forming PS-b-PMMA.

As part of the continuous effort towards DSA industrialization, IMEC and Tokyo Electron Limited (TEL) worked to implement DSA techniques for via patterning. The fabrication process was based on grapho-epitaxy with cylinder-forming PS-b-PMMA, with a focus on the key steps of BCP coating and pattern creation, as highlighted in figure 28. The enhancement of the resolution and thermal stability of the guide pattern was achieved by properly choosing the photoresist. Wet etching was considered a better option over dry etching due to its higher selectivity for PMMA removal. The combination of the highest quality photoresist, a neutral layer, and the wet etching method yielded the best hole pattern compared with other methods, and obtained around 75% size shrinkage [102].

Both grapho-epitaxy and chemo-epitaxy methods can be applied for hole shrinking, as reported by IMEC researchers [93, 103]. The work reported by TEL concentrated on improving the etch selectivity between the PS and PMMA blocks. The as-coated PS-b-PMMA film was exposed to UV radiation, during which the PS block was hardened through a cross-linking process, and the PMMA block was cleaved. The UV-treated PMMA block was more easily developed during wet-etching while the PS block was unaffected. The effect of the UV treatment was also confirmed in the work of Tiron et al., in which grapho-epitaxy-based DSA with cylinder-forming
Figure 31. Device structure of NiO resistive memory that incorporates self-assembled SiO$_x$ nanostructures. (a) Schematic of NiO memory with SiO$_x$-NDs and its operating mechanism through Ni CFs. The top electrode (TE), active layer, and bottom electrode (BE) are Pt, NiO, and Ni, respectively. Self-assembled SiO$_x$-NDs are formed by solvent annealing and plasma etching of Si-containing PS-$b$-PDMS BCPs. (b) Optical image of a 16 $\times$ 16 cell array for NiO resistive memories. The inset shows the unit cell of memories with 10 $\times$ 10 $\mu$m$^2$ cell area. (c) Cross-sectional SEM image of NiO resistive memory with SiO$_x$-NDs. The insets are SEM and TEM topview images of hexagonally formed SiO$_x$-NDs on NiO films before TE (Pt/Ti) deposition. Reprinted with permission from [114]. Copyright (2014) American Chemical Society.

PS-$b$-PMMA was implemented on a 300 mm wafer line in LETI with Arkema materials for hole shrinking [104]. In their work, different processing methods, such as wet etching, plasma etching, and a combination of wet etching and UV treatment, were compared for PMMA removal to create a PS mask. The best performance was obtained with the combination of UV treatment and wet etching [105].

4.2.2. Defect analysis. Similar to the case of line/space patterning, defectivity is also a great concern for DSA-based hole patterning. The research group from Taiwan Semiconductor Manufacturing Company (TSMC) utilized a lamellae-forming PS-$b$-PMMA system with the graphoepitaxy flow to analyze different types of defects and apply improvements to reduce the defect density [106]. The general types of defects, such as fall-on defects, residues, and blind holes, and the defect level of each were identified. The fall-on and residue defects were mostly intrinsic and were reduced by better filtration processes. Defect density drops from 353 to 117 defects/wafer after applying an updated filtration method. Blind hole defects were the primary concern. Blind hole defects were influenced by various process parameters, including the condition of the neutral layer, treatment of the guide pattern, and bake time. Optimization of these key steps significantly reduced the quantity of blind hole defects (from around 40 to less than...
Figure 32. Device reliability evaluations and resistance state distributions in NiO resistive memories with or without SiO$_x$-NDs. Write endurance results by DC sweeping mode in (a) the conventional cell and (b) the cell employing SiO$_x$-NDs. Cumulative probability graphs of resistance states (c) in 100 cells and (d) in various electrode areas without/with SiO$_x$-NDs. (e) Endurance performance of NiO memory cell ($10 \times 10 \mu m^2$) with SiO$_x$-NDs by using a reset pulse (100 $\mu$s) and a set pulse (500 ns). (f) Retention measurement of NiO memory cell ($10 \times 10 \mu m^2$) with SiO$_x$-NDs. The read voltage for all resistance measurements is 0.3 V. Reprinted with permission from [114]. Copyright (2014) American Chemical Society.

Figure 33. Procedure for patterning the top electrode. A self-assembled BCP template was adopted for pattern transfer with a lift-off process. Reprinted with permission from [116]. Copyright (2015) American Chemical Society.
Figure 34. Hybrid DSA with overlay control to fabricate a servo-integrated BPM template, by combining DSA, NIL, and optical lithography. (a) Prepatterns in both the data field and servo field defined by NIL. (b) First overlay to protect the servo field, followed by resist thinning and LTG in the data field. (c) Pattern transfer in the data field and second overlay to protect the data field, followed by HTG in the servo field. (d) BPM template with embedded servo. Reprinted with permission from [119]. Copyright (2014) American Chemical Society.
10 defects wafer$^{-1}$). Tiron et al also reported an improvement of blind hole defects though tuning the critical dimensions of the guide pattern [104].

Overall, there are still some concerns about applying DSA technology for hole patterning, given that BCPs are highly sensitive to the surface properties, as well as the geometric size of the guide resist. In addition, the occurrence of intrinsic defects which cannot be easily eliminated, and also the need for new design rules, are all under consideration. Regardless of these concerns, DSA is still considered a promising hole patterning technique with the potential to improve pattern uniformity and overcome challenges in sub-30 nm even sub-20 nm hole patterning.

5. Applications of BCP based nanopatterning

DSA is a high-resolution and cost-effective nanopatterning technique. When combined with conventional lithography, such as 193 nm immersion, DSA is capable of fabricating patterns with feature sizes <10 nm. As illustrated in section 4, DSA showed excellent performance on a 300 nm wafer production line as its first step towards industrialization. Several research institutions recognize the advantages of DSA and are seeking to use it for microelectronics manufacturing. So far, DSA of BCPs has been used in the fabrication of various semiconductor devices, such as fin field effect transistors (FinFETs), memory devices, and photonic devices. In this chapter, we review recent developments of DSA in device fabrication.

5.1. FinFET fabrication

FinFET was invented in 2001 to meet the stringent requirements of device scaling and performance enhancement in the semiconductor industry [107]. Sub-10 nm patterning with conventional lithography is extremely difficult. DSA has emerged as a promising alternative method for fin fabrication. For example, Liu et al demonstrated the complete process of graphoepitaxy-based DSA for fin fabrication at 29 nm pitch and evaluated the process parameters that affected the pattern transfer quality (figure 29) [108, 109]. Tsai et al compared the fin patterns obtained using PS-b-PMMA and high $\chi$ BCP at 24 nm pitch. It was observed that better line edge roughness and line width roughness were achieved with high $\chi$ BCP.

The IMEC group presented two strategies for fin fabrication using DSA chemo-epitaxy, a ‘Cut 1st’ hard mask approach and a ‘Cut-Last’ approach. In this work, the Cut 1st hard mask approach was considered the better method, because it was less harmful to the alignment mark and exhibited better overlay accuracy [110]. The integration of BCP-based nanopatterning into FinFET fabrication requires the co-optimization of the process, design, and layout. Some simulation work has been carried out to find optimal designs for the guide pattern mask, fin, and via structures [111, 112]. To date, DSA has demonstrated good capabilities in dense line/space patterning. When combined with other nanopatterning techniques, such as EUV and EBL, DSA can easily realize sub-10 nm patterning. The on-going miniaturization of device feature size requires that high $\chi$ BCPs be incorporated in DSA, which
wou would bring some positive improvement for device fabrication (i.e. improved LER/LWR).

5.2. Memory fabrication

Memory devices are scaling as fast as CMOS, but usually have higher error tolerance. This relaxes constraints such as defectivity and overlay. Unlike in previous examples, where DSA was utilized to pattern a key structure (i.e. a fin) in a device, for memory fabrication, BCP is used to form a porous insulating layer inserted between the top electrode and the functioning layer, which is not usually included in the initial device structure. It was found that the electrical performance of novel memory devices, such as phase change memory (PCM) and resistive random access memory (RRAM), can be significantly improved by inserting a nanostructure layer between the top electrode and the functioning layer. DSA is an ideal method for preparing a regular, periodic nanostructure. For instance, in the work presented by Park et al., an SiO$_x$ layer made from a silicon-containing BCP was deposited between a TiN electrode and a phase change Ge$_2$Sb$_2$Te$_5$ (GST) thin film in a PCM device (figure 30), which dramatically reduced the switch power consumption of the device (20× reduction).

The main advantage of using a BCP as the intermediate layer is its ability to form various morphologies with controllable size, which enables tunable power reduction [113]. You et al implemented a BCP-generated SiO$_x$ layer in an RRAM device between a Pt top electrode and a Ni filament layer (figure 31), resulting in a reduction in set/reset voltage while minimizing the large variation of high resistance state (HRS) observed in the original device structure (figure 32) [114]. BCPs can also be used to fabricate the template for depositing nanoelectrodes in RRAM devices, as shown in figure 33 [115, 116]. These works demonstrate the use of DSA of BCPs in novel ways, not only in forming hard masks for pattern transfer but also as a performance-enhancing media.

5.3. Bit-patterned media fabrication

Conventional hard disk drives (HDD) utilize magnetic grains within the magnetic film for data storage. The reality that a dozen magnetic grains are required to store a single bit of data limits the enhancement of its storage density. Instead, bit-patterned media (BPM) has been proposed as a potential technology for increasing the storage density of future HDDs. This poses a great challenge for the fabrication process. The existing nanopatterning techniques (i.e. EBL) are either too expensive or too time consuming for fabricating BPM [117]. Sub-10 nm lithography is needed to define the resolution in the manufacturing of high-density storage units.

For a long period, DSA was the only option for BPM fabrication of densities greater than 1.5 Tb in$^{-2}$. Early efforts to use DSA for bit patterning included using cylinder- or sphere-forming BCPs to directly pattern the magnetic thin film. Combining DSA with EBL to acquire rectangular dots. The detailed summary of these early works can be found in a previous review paper [118]. A more popular method of bit patterning involves using DSA to make a nanoimprint template and then create thousands of replicas for high-volume patterning on a media layer. For instance Kuo’s group used two types of BCPs, cylinder-forming PS-b-PMMA and sphere-forming PS-b-PDMS, to produce integrated templates with both servo and data zones, achieving an area density of 1 Tb in$^{-2}$ and 1.5 Tb in$^{-2}$, respectively. In both cases, a nanoimprint technique was used to create the pre-pattern for DSA, as depicted in figure 34 [119–121]. In another work reported by Doerk et al from Western Digital, self-aligned double patterning (SADP) was applied on an as-produced BCP pattern to achieve sub-10 nm feature size with successful pattern transfer into the silicon substrate [122]. Xiong et al proposed an alternative method of making BPM templates, in which a lamellae-forming triblock copolymer, P2VP-b-PS-b-P2VP, was employed to make two BPM templates: one with a circumferential pattern and the other with a radical pattern, as shown in figure 35 [123]. The complete rectangular bit pattern was obtained by overlapping these two masks. These works explore common methods of fabricating BPM templates. DSA followed by nanoimprinting is an efficient, low-cost method. DSA of PS-b-PMMA combined with SADP promises sub-10 nm resolution.

5.4. Photonic device fabrication

In recent years, researchers have extended the use of BCP-based patterning to the fabrication of photonic devices. It is widely recognized that nanostructures with dimensions smaller than the wavelength of light have a profound impact on the optical properties of photonic devices. There are several interesting examples of the use of high χ BCP to make photonic nanostructures. For example, Hulkkonen et al utilized poly(styrene-block-poly(2-vinylpyridine)) (PS-b-P2VP) to make a template for producing a porous silicon structure, as shown in figure 36. The size of the obtained silicon pores could be tuned by varying the etch time during the dry etch process (figure 36). Different values of the refractive index and reflectance were attained by tuning the silicon pore size [124]. Tabari et al also employed PS-b-P2VP to create a cylindrical mask for deposition of silicon nano-pillars with a high aspect ratio. These silicon nano-pillar arrays formed an anti-reflective layer, whose reflectance of visible light decreased with increased pillar height [125]. In another work, Rasapa et al reported using PS-b-PDMS-based patterning to make silicon nanofin arrays on a silicon wafer or an SOI substrate. The as-fabricated dense arrays of silicon nanofins were used as a filter for a guided mode resonator with sensitivity enhancement [126]. In general, the employment of BCP-based nanopatterning provides a cost-effective method of manufacturing sub-wavelength nanostructures for photonic devices with high scalability and reproducibility.

6. Conclusion and outlook

In this paper, we reviewed the recent progress of DSA technology for sub-10 nm patterning, in the context of microelectronic fabrication. DSA combines top-down lithography
and bottom-up molecular assembly, which enables low-cost, high-throughput manufacturing. DSA based on chemoepitaxy and graphoepitaxy can achieve high-resolution patterning, which is hardly accessible with traditional lithography. Since 2017, DSA has been listed in IRDS as a complementary technique to EUV lithography for hole shrinking, logic device fabrication, and nanowire patterning. Several years ago, IMEC developed the DSA process on a 300 mm wafer fabrication line as the first step towards DSA industrialization, by seeing the lower cost-of-ownership of DSA in comparison to multipatterning techniques. Controlling the defectivity of DSA (mainly dislocations and bridges between lines) has been a great challenge. However, research efforts into the kinetics of defect annihilation indicate that DSA can achieve defectivity levels below 10 per cm², making DSA relevant for volume manufacturing. In the fabrication of bit patterned media or memory devices, DSA holds a significant advantage since the structure is simply periodic, and the defectivity requirement is not as stringent.

During the last decade, tremendous efforts have also been made to enhance the quality of BCP material and improve the process methodology. So far, PS-b-PMMA-based DSA has been thoroughly studied and applied to device fabrication. Liu et al reported using DSA with PS-b-PMMA for sub-10 nm FinFET fabrication. It is worth noting that the half-pitch size in the DSA field differs from the definition of a technical node in the semiconductor industry. For a lamellar morphology, the full pitch is twice the half-pitch; and in the case of cylindrical morphology, the duty cycle is about 30%. Even though the current PS-b-PMMA system can fulfill fabrication at the 7 nm logic node (sub-15 nm patterning), a variety of high χ BCPs have been developed to further enhance DSA patterning resolution (e.g. sub-5 nm patterning). Different processing techniques, such as the topcoat method and solvent annealing, have been used to promote the self-assembly process of high χ BCPs. Derived from the DSA field, the SIS technique has recently been adopted in EUV lithography to enhance the pattern transfer process. DSA is believed to have promising potential in fabricating emerging nanodevices, such as the high-density crossbar array devices (with applications in neuromorphic computing), and for back-end-of-line (BEOL) processes. Although we have not covered the application of DSA in areas than the semiconductor industry, membranes with high porosity at nanoscale have been developed with BCPs at relatively low cost. Overall, DSA is capable of creating sophisticated nanostructures by manipulating the magic BCP materials. Many of the insights and innovations originating from DSA will also benefit the chemistry and biological applications (e.g. water filtering and drug delivery) of BCPs, for years to come.

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