1 Introduction

Advances in lithography have always been critical in the drive toward each subsequent semiconductor node. By anticipating limitations in the scaling ability of immersion lithography, the industry has been pursuing next-generation lithography techniques beyond multiple patterning. Several techniques have been proposed, including extreme-ultraviolet (EUV) lithography, multibeam electron-beam lithography, nanoimprint lithography, and directed self-assembly (DSA) of block copolymers (BCPs). DSA has attracted a great deal of interest from major semiconductor manufacturers for several years following its initial demonstrations in the early 2000s. Since then, several methods or process flows for using DSA have been proposed by various groups.

The purpose of this Spotlight is to compile various methods in one publication. The acronyms and naming conventions used in various publications can also be confusing for anyone who needs a concise description of the methods available. Another goal of this publication is to provide an easy-to-follow reference for lithographers who are interested in learning or using DSA for patterning. It is written for the nonchemist in mind or someone who has no familiarity with the DSA process; however, sufficient details are provided to follow and understand the steps.

2 Directed Self-Assembly and Block Copolymers

DSA is a process in which a BCP is guided and allowed to assemble itself to form structures on a substrate without using traditional patterning techniques.

In most lithography processes (except for e-beam and imprint patterning, which are maskless), the mask defines the printed pattern. In DSA, a prepatter can be formed using traditional lithography; however, the final target critical dimension (CD) is defined by the BCP. Some call this approach “CD in a bottle” because the dimensions are predefined by the BCP composition. The most commonly used BCP combines polystyrene (PS) and poly(methylmethacrylate) (PMMA) into two distinct blocks in a polymer chain. The biggest difference between random copolymers and BCPs is that the latter have polymer blocks composed of only one monomer and are not randomly distributed along the polymer chain. Figure 1 shows the structural differences between random copolymers and BCPs of PS and PMMA.

The BCP composition determines the CD dimensions, shapes that can be achieved, domain orientation, and overall pattern formation process. The primary physical parameters to be controlled are monomer types, monomer ratios used, molecular weight ($M_w$), polydispersity (PD), overall organic purity of the BCP, and interaction parameter ($\chi$). The effect of these parameters in pattern formation will be discussed briefly in the following sections.

When two monomers with different polarities are assembled into a BCP, they need to naturally segregate themselves into microphases forming well-ordered domains. An analogous process is the combination of water and oil. Polymer
known as a fingerprint pattern. Later, discussions on DSA flows will address how to align the patterns in an organized fashion.

BCP molecular weight and polydispersity are important properties for controlling CD and pitch. The pitch illustrated in Fig. 3 is related to the polymer chain length $L_o$ value. $L_o$ is related to the total degree of polymerization for each block, which means that the length of each block controlled by the number of monomers in each block is the determining factor for pitch. Figure 5 illustrates how a BCP assembles to form defined CD and pitch. Two polymer chains with similar chain ends interact to define the CD (shown as either blue or red domains). Because the hydrophobic block of the BCP does not interact with the hydrophilic block, the two blue ends of the BCP in Fig. 5 must interact with each other. Polydispersity, the measure of the distribution of molecular mass in a given polymer, is critical for obtaining consistent CD and pitch without defects or variations. Ideally, all of the chain lengths in a BCP must have the same number of atoms. If some polymer chains are longer than others, imperfections on the assembly can occur.

As briefly mentioned earlier, a factor influencing spacing is the ability of each block in the BCP to segregate into its own domain. The larger the interaction parameter ($\chi$) between the blocks is, the easier it is for the two chains to assemble into their own domains, even when the chains are smaller, which means that smaller CD and pitch can be achieved with shorter polymers. However, their Flory interaction parameter must be larger than for longer chain polymers. The product of $\chi$ and the segment length ($N$), therefore, determines the spacing of the ordered structure. The higher the value of $\chi$ is, the finer the pitch of the resulting structure can be. Standard PS-$b$-PMMA materials have relatively low $\chi$, which limits the pitch to 20 nm or larger. New chemistries other than PS-$b$-PMMA to produce high-$\chi$ BCPs are being developed, for example, replacing the PMMA component with polydimethylsiloxane$^{3,4}$ or polyhydroxystyrene$^2$ or other inorganic monomers.$^5$ Modifying PS-$b$-PMMA is another approach to increase $\chi$. In this manner, it is possible to tune $\chi$, the molecular weight, and the glass transition

Figure 5 Scanning electron micrograph and illustration of a BCP after thermal annealing and phase separation. The large gray blocks are resist lines. Smaller line/space structures form in the trenches between the resist blocks. Two polymer chains are required to define CD.
neutral to either block, otherwise the block aligning to the wall will also cover the bottom surface, preventing removal of the other polymer block all the way through the substrate during pattern transfer.

Graphoepitaxial flows can be classified into two categories, depending on whether a pattern is to be shrunk or if pitch multiplication is desired. There are flows to shrink a contact hole pattern, multiply a contact hole pattern or a line/space pattern, or form holes inside trenches. However, this process has found the most promising approach for reducing contact hole sizes. Figure 7 shows the possible structures that can be achieved using this process.

3.1.1 Contact holes
The process of obtaining a smaller-dimension hole pattern from a larger one includes producing a larger prepattern or hole using common lithographic techniques. After the prepattern is formed, there are two options, depending on the resist used. If the resist is not soluble in the solvent used by the BCP, one could coat the BCP directly on top of the resist, anneal the BCP to allow it to separate into its different domains, and then remove the core or center of the BCP structure. Removal of the BCP central polymer can be done by reactive ion etching (RIE) or a wet development process. Both methods have been compared. The process is illustrated in Fig. 8.
amine groups, and these become affine to the PMMA block in PS-\textit{b}-PMMA BCP.\textsuperscript{33}

In another study, neither a guiding nor a brush layer was used to induce alignment. Instead of a magnetic field and cooling below the order–disorder transition temperature of a BCP, a homopolymer blend was used to induce alignment. This resulted in hexagonally aligned holes.\textsuperscript{34}

There have been reports of combining a neutral layer and hardmask into one layer. The bifunctional layer performs two tasks: it provides a neutral surface for the BCP to separate and offers hardmasking capabilities for pattern transfer. The hardmask–neutral layer approach was demonstrated in a graphoexpitaxy flow for line/space patterning\textsuperscript{35} and contact holes.\textsuperscript{10,36}

\section{4 Combining Grapho- and Chemoepitaxial Flows}

Early demonstration of combining grapho- and chemoepitaxial flows to create subresolution patterns was presented by a group from Korea.\textsuperscript{37} In this process, a graphoexpitaxy pattern is converted to a chemical-epitaxy pattern. After coating a neutral layer on a substrate, i-line patterning is used to form trenches with a pitch of 600 to 1000 nm. A PS-\textit{b}-PMMA BCP was assembled within the trenches to create an ordered array of lines and spaces. Using oxygen plasma, the PMMA
mitigation. A couple of studies have looked into this question.\textsuperscript{54,55} In order to probe answers to this question, the effect of BCP annealing temperature and time becomes the most important factor.

Increasing the annealing temperature increases the rate at which the BCP reaches equilibrium. This reduces dislocation and bridging type defects. There is a balance between temperature and time. At higher temperatures, the annealing can be done in a shorter time. One must keep in mind the decomposition temperature of the BCP. There is at least one report that shows that the pitch of the BCP can change with annealing temperature.\textsuperscript{56} This being the case, the temperature versus pitch profile for a BCP must be characterized before attempting optimization of lamellar DSA processes. A pitch that is not commensurable with the chemical guide or graphoepitaxy CD can produce dislocations.

Theoretically and experimentally, dislocations can be completely eliminated with long annealing times;\textsuperscript{55} however, the times required may be too long to be practically useful in semiconductor fabrication (Fig. 25(a)). On the other hand, bridging defects, particularly one period that bridges between two lines, have shown weak annihilation behavior as a function of annealing time and experimentally, complete removal of these has not been achieved even with long annealing times.\textsuperscript{55} Potential sources of these defects are material impurities, volume fraction differences on the BCP, or processing-induced particles. Recently, bridging was connected to the mismatch in height between the guiding layer and the neutral layer. When the guiding layer is much taller than the neutral layer, the chemical template is disrupted, and bridge defects appear.\textsuperscript{57}

The kinetics of defect annihilation is affected by film thickness.\textsuperscript{55} Bridging-type defects are lower with thinner BCP thickness (Fig. 25(b)). In a study, while bridging defects were observed at 22-nm thickness, defects decreased by orders of magnitude at thicknesses >35 nm. However, the dislocation density is higher.

![Figure 25](image)

\textbf{Figure 25} (a) Impact anneal temperature and (b) film thickness on dislocation defects. Reproduced from Ref. 55.