Recent Achievements in Sub-10 nm DSA Lithography for Line/Space Patterning

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Silicon-containing and modified PS-b-PMMA high-$\chi$ block copolymers materials were produced to achieve lamellar mesostructure as low as 14 nm intrinsic period ($L_0$) and ordered by graphoepitaxy or chemoepitaxy processes. Line Edge Roughness (LER) measurements of 2.5 nm (3 $\sigma$) can be extracted from CD-SEM pictures of poly[(1,1-dimethyl silacyclobutane)-b-styrene] after etching step. Materials integrations on a 300 mm track process are highlighted. In fingerprint, new BCPs LWR L/S values are 1.5/1.1 nm in comparison to a graphoepitaxy flow where the LWR L/S values are 2.0/1.1 nm. Alternative methods to create high-resolution guiding patterns for directed self-assembly of block co-polymers and the scale-up to obtain industrial BCPs meeting electronic requirement are also reported.

Keywords: Lithography, Block copolymer, High segregation strength, Directed self-assembly, Graphoepitaxy, Chemoepitaxy

1. Introduction

The creation of ordered structures at the nanometer-length scale drives many fields of science with the implicit challenge of feature size reduction obtained from self-assembled systems. Among the materials of choice, block copolymers (BCPs) provide an exquisite route for the definition of nanostructures with controlled periodicity. Intense efforts are currently devoted to directed self-assembly (DSA) of BCPs with applications in the lithographic industry. BCP nanostructures obtained through bottom-up methodologies are useful for the definition of well-ordered 2D arrays in the thin film configuration. These nano-patterns are subsequently used as masks for the definition of elementary features such as vias or interconnects.

Poly[styrene-b-(methyl methacrylate)] (PS-b-PMMA) constitutes the standard material for this application since methodologies to control the BCP self-assembly (i.e. combination of DSA with top-down techniques such as conventional photolithography and electron-beam lithography) are well-established. The graphoepitaxy [1-4] and/or chemoepitaxy [5,6] techniques addresses the problem of the long-range ordering of features while the control of the surface energies at the BCP thin film interface is commonly obtained through the use of grafted sub-layers [7] or top coats [8]. This combination has led to technological breakthroughs allowing the introduction of DSA of BCPs in the microelectronic industry. A significant advantage of the PS-b-PMMA system is that the PS
and PMMA blocks, have nearly equal surface energy at common annealing temperatures, thus a top-coat approach can be avoided with this particular system [9]. Nevertheless, PS-b-PMMA BCPs suffer from a relatively low Flory-Huggins parameter, $\chi$, thus limiting the microphase separation length scale to about 20 nm [10]. To pursue the onward progress towards miniaturization, BCPs with higher $\chi$ are required as low molecular weight BCPs could resolve sub-10 nm features for sufficient segregation strength (i.e. $\chi N > 10.5$, where $\chi$ is the Flory-Huggins parameter and $N$ the degree of polymerization) [11]. In this paper, we will discuss such BCPs design and the scale-up to obtain industrial materials meeting electronic requirements thanks to Arkema and Brewer Science Inc. partnership, with results of their ordering by graphoepitaxy or chemoepitaxy process. High $\chi$ material integration on a 300 mm track process will be reported as well as alternative methods to create high-resolution guiding patterns, where sub-10 nm dimensional accuracy will be required to properly achieve optimal DSA patterns.

2. Results and discussions

2.1. Silicon containing high $\chi$ block copolymers

Recently we have designed a new block copolymer system, i.e. poly(1,1-dimethyl-silacyclobutane-b-styrene) (PDMSB-b-PS), enabling the production of highly ordered patterns with sub-10-nm features. In order to get the well-defined polymer with controlled molecular weights and compositions, anionic polymerization was performed by sequential addition of monomers in polar media using sec-BuLi as initiator. (See Fig. 1. for the macromolecular structure of the PDMSB-b-PS).

![Fig. 1. Macromolecular structure of the PDMSB-b-PS block copolymers (m and n respectively denote the degree of polymerization of the PDMSB and PS blocks).](image)

Table 1. Macromolecular parameters and morphological characteristics of PDMSB-b-PS copolymers

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_\text{n}$ (kg/mol)</th>
<th>$D^\text{a}$</th>
<th>$\beta$ (PDMSB)$^b$</th>
<th>Morphology$^c$</th>
<th>$d^d$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMSB$<em>{88}$-b-PS$</em>{78}$</td>
<td>16.9</td>
<td>1.10</td>
<td>0.52</td>
<td>Lam</td>
<td>25.2</td>
</tr>
<tr>
<td>PDMSB$<em>{78}$-b-PS$</em>{130}$</td>
<td>21.5</td>
<td>1.08</td>
<td>0.28</td>
<td>Hex</td>
<td>19.8</td>
</tr>
<tr>
<td>PDMSB$<em>{60}$-b-PS$</em>{54}$</td>
<td>11.6</td>
<td>1.10</td>
<td>0.5</td>
<td>Lam</td>
<td>18.1</td>
</tr>
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</table>

$^a$ Determined by SEC in CHCl$_3$ at 25°C using the universal calibration technique. $^b$ Determined using $^1$H-NMR in CDCl$_3$ using the bulk homopolymer densities at 140°C ($\rho_{\text{DMSB}} = 0.86$ g/cm$^3$, $\rho_{\text{MMA}} = 1.13$ g/cm$^3$). $^c$ Morphological assignments (Lam: lamellar, Hex: hexagonally packed cylinders) and domain spacing (d) Determined using SAXS data at $T = 140°C$.

Synchrotron SAXS powder patterns acquired at 140 °C are reported in Fig. 2 for PDMSB-b-PS copolymers. The SAXS reflections for PDMSB$_{88}$-b-PS$_{78}$ and PDMSB$_{60}$-b-PS$_{54}$ obtained at 140 °C are consistent with a lamellar mesostructure with a series of peaks at scattering wave vectors indexed as $q/q^* = 1, 2, 3, 4, 5$. Decreasing the PDMSB volume fraction leads to a PDMSB hexagonally packed cylinders mesostructure for PDMSB$_{78}$-b-PS$_{130}$ with a series of peaks at scattering wave vectors indexed as $q/q^* = 1, 3^{1/2}, 2, 7^{1/2}, 3$.

![Fig. 2. Synchrotron SAXS profiles acquired at 140 °C for PDMSB$_{88}$-b-PS$_{78}$, PDMSB$_{78}$-b-PS$_{130}$ and PDMSB$_{60}$-b-PS$_{54}$ samples.](image)
commensurable with the polymer periodicity measured by SAXS (in this case to be 23 nm). This integration scheme allows well-organized lamellae into trenches with a height of 80 nm. The preferential wetting of one block at the bottom of the trenches can be avoided thanks to a tight control of the dimensions of the guiding lines and by a good wetting of the PS block onto the SoC sidewalls.

![Fig. 3. STEM cross-section of graphoepitaxy CSS type polymer (120 nm high, 90 nm wide trenches).](image)

Such a mask can then be processed by plasma. In a first step, a non-selective fluorine-based chemistry is used to remove the upper parallel lamellas coming from a preferential attraction of one block with the ambient atmosphere. A second oxygen-based chemistry is used to remove selectively the PS block and oxidize the PDMSB phase. After these steps, some preliminary Line Edge Roughness (LER) measurements can be performed. Depending on duration of the non-selective etching step as illustrated in Fig.4 and Fig. 5, different values are measured. In best cases, a LER of about 2.5 nm (3 σ) can be extracted from these CD-SEM pictures.

![Fig. 4. LER measurements on oxidized PDMSB lamellas after a non-selective planarization etching step and 2 different etching times for the selective removal of the PS block.](image)

2.2. Modified PS-b-PMMA high-χ block copolymers

Brewer Science’s modified PS-b-PMMA BCP materials are di-block copolymers with organic polymer blocks, e.g., PS and PMMA analogues, which can be easily synthesized by controlled radical polymerization techniques. A variety of functional groups can be incorporated into the polymers to obtain the desired functionalities of balanced surface energy of the polymer blocks, tunable glass transition temperatures ($T_g$) and $\chi$ values. The block copolymers have similar chemical and physical properties to standard PS-b-PMMA. The similarity in the thermal properties and stability with PS-b-PMMA enables application of similar thermal annealing processing conditions and procedures of standard PS-b-PMMA. The $\chi$ and molecular weight can be tuned to achieve a $L_0$ range of 14-40 nm for lamellae-forming BCPs. Figure 6 shows the SEM images (top-down) of some representative materials. No solvent annealing or topcoat were needed even for small pitch sizes such as 14 nm.

![Fig. 6. SEM images of representative modified PS-b-PMMA materials (scale bar 100 nm).](image)

Some modifications were performed to improve the kinetics of BCP self-assembly during thermal annealing to remove defects. The major difference with these new BCPs is their lower and tunable $T_g$ for the two constituting blocks. Our hypothesis is that the enhanced polymer chain mobility achieved by decreasing the $T_g$ of the block copolymers could help with improving the kinetics of BCP self-assembly during the thermal annealing.
Figure 7 presents some preliminary experimental results that support our hypothesis and shows SEM images of B-L18 (18 nm \( L_0 \)) and T-L18 (18 nm \( L_0 \)), and the comparison of their defect density from the analysis of fingerprint SEM images. It can be seen that T-L18 has significantly lower fingerprint defect density than B-L18, which we attribute to the lower \( T_g \) of T-L18 as well.

![SEM images of B-L18 and T-L18](image)

**Fig. 7.** SEM images of B-L18 and T-L18 annealed at 180 °C for 5 min, and their fingerprint defect density.

2.3. High \( \chi \) material integration on a 300 mm track process

High \( \chi \) organic lamellar-forming block copolymers with 18 nm intrinsic period \( (L_0) \) value were evaluated on both un-patterned and patterned surfaces (fingerprint and grapho-epitaxy configurations).

Using a 300 mm SCREEN DUO track, a neutral layer (NL) was first coated on 300 mm bare silicon wafers, baked to 250 °C for 5 min and then rinsed with PGMEA. Afterwards, the BCP was coated and then thermally annealed. Vertically oriented lamellae were successfully obtained without using a top-coat. BCP film thickness uniformity was characterized using ellipsometry over 49 measurement points.

For a mean BCP thickness of 19.7 nm, 3 sigma of 1.2 nm was obtained. Mean thickness and 3 sigma of the brush layer were measured to 5.7 nm and 0.5 nm, respectively.

It is also worth-mentioning that there is no dewetted area observed on the surface over the whole wafer. Process temperatures and times were varied to determine the best self-assembly annealing conditions allowing lower fingerprint defectivity. Different temperatures were investigated from 140 °C to 220 °C for a fixed time of 5 min.

For intrinsic period extraction and fingerprint defectivity analysis, CD-SEM inspection using a Hitachi CG4000 or 6300 scanning electron microscope (SEM) and off-line image treatment using an in-house developed software were carried out. The BCP natural period was measured to 17.9 nm with a good uniformity of 3 \( \sigma = 3% \) over different locations on the wafer. Following the methodology previously described [13,14], the fingerprint defectivity allowed us to get information about the range ordering length and thus the self-assembly kinetics of the BCP. There were primarily 3 types of defects analyzed: junction blocks, end of lines and singular defects as illustrated in the inset of Fig. 8. One of the main contributors to defect formation was annealing temperature (Fig. 8). In general, defect formation decreases with increasing annealing temperature up to an optimum. Once the optimum temperature is reached, higher temperature can degrade the polymer and defect formation increases once again. The optimum annealing temperature was 180 °C.

![Fingerprint defectivity analysis](image)

**Fig. 8.** Fingerprint defectivity analysis: Fingerprint defect density measurement across different annealing temperatures at a constant time. The inset shows a raw SEM image and its corresponding binarized image with the three types of monitored defects for a fingerprint patterns.

Alignment in a grapho-epitaxy test vehicle was also evaluated using the high \( \chi \) BCP. Graphoepitaxy silicon oxide pre-patterns were prepared using 193-nm immersion lithography and subsequent dry etching through a typical organic Si-containing antireflective coating, spin on carbon hard mask [15]. Trenches of different widths ranging from 100 nm to 200 nm were used to determine the pitch multiplication capabilities. The SEM images after coating and thermal annealing are shown in Fig. 9 below. It was demonstrated that \( x4 \) – \( x7 \) multiplications were reached with a pitch of 17.9 nm.

In fingerprint, new BCPs LWR L/S values are 1.5/1.1 nm in comparison to a graphoepitaxy flow where the LWR L/S values are 2.0/1.1 nm (as reported in Table 2). To further optimize such
values, we decided to develop methods to create higher resolution guiding patterns.

<table>
<thead>
<tr>
<th>MF = 4</th>
<th>MF = 7</th>
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<tbody>
<tr>
<td><img src="image1.png" alt="SEM images" /></td>
<td><img src="image2.png" alt="SEM images" /></td>
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</table>

Fig. 9. SEM images of grapho-epitaxy vehicles after BCP coating and thermal annealing. MF refers to as the multiplication factor: the guiding CD to the \( L_0 \) ratio.

Table 2. Comparison between High \( \chi \) values from fingerprint and graphoeptaxy flows

2.4. Alternative methods to create high-resolution guiding patterns for directed self-assembly of block co-polymers

One of the most suitable methods for direct self-assembly (DSA) of block copolymers (BCP) consists of creating chemical patterns on the top of a polymer brush layer. By properly tuning the chemical affinity between the brush layer and the BCP domains, highly oriented and ordered structures can be achieved. The most commonly used techniques to create chemical guiding patterns are based on creating a mask on top of the brush layer and using it for a selective etching or chemical functionalization. Usually, DUV optical lithography or electron beam lithography are employed. However, both methods present limitations in terms of resolution. DUV optical lithography provides high throughput, but resolution below 50 nm can only be achieved by immersion, adding extreme complexity and cost to the process. Alternatively, electron beam lithography can ensure higher resolution, but still in this case, proximity effects preclude the creation of very dense guiding patterns.

We have developed novel approaches for the creation of chemical guiding patterns on PS-OH brush layers to direct the self-assembly of lamella forming PS-\( b \)-PMMA. [16]. They are different forms of direct writing, presenting the advantage of being resistless, simplifying the overall guiding pattern creation procedure. In the first approach, chemical guiding stripes are created directly on a PS-OH brush layer by exposing it to electrons (Fig. 10 a) [17]. Typically, large electron doses are required (between 10 mC/cm\(^2\) and 1,000 mC/cm\(^2\)) to induce a chemical contrast on the thin brush layer, as a consequence of the cross-linking of PS molecules. Although PS is usually resistant to electron beams, beyond a certain e-beam dose it undergoes cross-linking, through the breakage of the phenyl groups.

The second set of methods are based on scanning probe lithography (SPL) [18], in which the guiding patterns are created by the tip of an atomic force microscope (AFM). In this case, the absence of proximity effects and the very small dimensions of the AFM tip allow obtaining chemical guiding patterns with linewidth below 10 nm. We have explored to ways of using SPL to create chemical guiding patterns: (i) inducing the local oxidation of PS-OH brush layers under the application of a voltage (Fig. 10 b) [19]; and (ii), by thermal-SPL [20], where the AFM tip is heated to locally evaporate a thin resist. The two key steps of this second process are the accurate patterning of a poly(phthalaldehyde) resist layer of only 3.5 nm thickness, and the subsequent oxygen-plasma functionalization of the underlying PS brush layer.

We have also recently investigated the creation of topographic guiding patterns by EUV interference lithography [21]. In this case, EUV is used to expose an HSQ resist. After development, the resulting guiding patterns consist of SiO\(_2\) stripes of 70 nm in height, with a tunable width down to 50 nm. The major advantage of this method is the extremely low line edge roughness of the guiding patterns. We envision that these methods will be highly valuable for the investigation of the DSA behavior of novel high-chi materials, where sub-10 nm dimensional accuracy will be required to properly achieve optimal DSA patterns.
Fig. 10. Directed Self Assembly of PS-b-PMMA by chemical epitaxy by two high resolution, direct writing (resistless) methods. (a) Electron beam direct exposure; (b) local oxidation by scanning probe lithography. In both panels, the SEM images show the PS patterns after the DSA process and removing the PMMA block. The inset sketches the process to create the guiding patterns.

2.5. Scale-up to obtain industrial BCPs meeting electronic requirements

Arkema has proved itself in the manufacturing of high volume of perfectly reproducible PS-b-PMMA block copolymers for DSA application. A whole range of products were developed from 20 to 50 nm in lamellar and cylindrical morphologies under the trade name of Nanostrength® EO. Producing high volume of high $\chi$ materials like PDMSB-b-PS is a new challenge. Lab synthesis is performed in THF at -70 °C. THF is a very hygroscopic solvent and needs to be drastically water-purified for anionic polymerization (Table 3). Low temperatures are difficult and expensive to achieve on large batches. Arkema has developed the right additives to be able to perform the synthesis at ambient temperature in toluene, an apolar solvent (Table 3).

Another challenge is the metal decontamination to meet electronic requirements. Arkema has adapted its PS-b-PMMA process for metal removal to PDMSB-b-PS. All the metals are currently below 10 ppb in the resist formulation. Arkema target is now below 1 ppb.

Arkema has registered this high $\chi$ material formulated as a resist under the trade name of Nanostrength® EO X2.

Table 3. Comparison of conditions of synthesis between lab and industry

<table>
<thead>
<tr>
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<th>Lab conditions</th>
<th>Industrial conditions</th>
</tr>
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<tbody>
<tr>
<td>Solvent</td>
<td>THF/Heptane mixture</td>
<td>Toluene + additives</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>-70</td>
<td>+20</td>
</tr>
</tbody>
</table>

3. Conclusion

Both silicon-containing and modified PS-b-PMMA high-$\chi$ block copolymers have been developed that retain the advantage of thermal annealing alone while simultaneously increasing the $\chi$ value to achieve a $L_0$ (block copolymer natural pitch) as low as 14 nm for lamellar-structured materials. They were ordered by graphoepitaxy process giving LER of 2.5 nm (3 $\sigma$) after etching step. Materials integrations on a 300 mm track process are highlighted. In fingerprint, new BCPs LWR L/S values are 1.5/1.1 nm in comparison to a graphoepitaxy flow where the LWR L/S values are 2.0/1.1 nm. Alternative methods to create high-resolution guiding patterns for directed self-assembly of block co-polymers and the scale-up to obtain industrial BCPs meeting electronic requirement are also reported.

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