Directed self-assembly of block copolymers on chemically nano-patterned surfaces

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Departament de Química

Universitat Autònoma de Barcelona

Laura Evangelio Araujo

DIRECTORS

Francesc Pérez Murano
Institut de Microelectrònica de Barcelona (IMB-CNM, CSIC)

Jordi Fraxedas Calduch
Institut Català de Nanociència i Nanotecnologia (ICN2)

TUTOR

Joan Bausells Roigé
Institut de Microelectrònica de Barcelona (IMB-CNM, CSIC)

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Chapter 3

Directed self-assembly of PS-\(b\)-PMMA block copolymers by chemical epitaxy

In directed self-assembly by chemical epitaxy, block copolymers are guided by chemical patterns created on the substrate. Thus, tuning the chemical interactions between the block copolymer domains and the chemical pattern, an optimal BCP alignment with high density multiplication factors can be achieved.

In this chapter, the development, optimization and characterization of a chemical epitaxy process based on substrate functionalization is presented. To demonstrate its industrial applicability, the process has been transferred to the cleanroom of CEA-Leti, which is more focused towards industrial production, and has a pilot line intended to the fabrication of CMOS integrated circuits.

On the other hand, two other novel approaches based on chemical direct writing techniques by means of electron beam lithography and atomic force microscopy lithography are presented.
3.1. Introduction to directed self-assembly of block copolymers by chemical epitaxy

DSA of BCPs is becoming a very promising approach to overcome the conflict between the continuous demanding to decrease the size of electronic devices and processing costs of traditional lithographic techniques, since it is a very effective and simple method to pattern dense arrays of features with dimensions in the nanoscale. Several recent studies have shown that DSA is an emerging technique that can be used to improve the line-width roughness (LWR) and line-edge roughness (LER), apart from enhancing the resolution of the currently patterning methods. Nevertheless, it remains a challenge to fulfill the rigorous requirements of defectivity from the semiconductor industries. Chemical and topographical guiding patterns provide highly oriented and ordered features, and have demonstrated to offer satisfying structures demanded by the semiconductor industry.

Chemical epitaxy consists of a combination of a top-down method to create chemical patterns with a self-assembled periodic process, which allows getting higher resolutions than the lithographic ones. In chemical epitaxy, the guiding patterns consist of guiding areas that prefer to be wetted by one of the domains of the BCP and that are separated by interspatial regions which are normally referred to as background areas. These guiding and background lines are characterized for having different interactions with the domains of the BCP. Therefore, in chemical epitaxy DSA, the chemistry and the guiding pattern geometries determine the generation of microstructures with the lowest free energy. Consequently, there has to be a high control of the thermodynamic forces which fine-tune the patterning order, by controlling the critical parameters on the fabrication of chemical guiding patterns.

Several materials can be used as background layers to create the guiding patterns: self-assembled monolayers, HSQ resist and end-grafted homopolymers or random copolymer brushes. The most widely used technique consists on using end-grafted homopolymers or random copolymer brushes. Different approaches are currently used to create the guiding patterns. The first chemoepitaxy approach based on substrate functionalization was presented by Kim et al. in 2003 where a self-assembled monolayer (SAM) was used to chemically create the guiding patterns. In this approach, the photoresist was patterned by EUV-IL, with alternating lines and spaces of period \( \text{L}_0 \), and then the topographic resist pattern was converted to a chemical pattern by irradiating the sample with X-rays. However, this method presents some disadvantages regarding the lithography step, since it has to nominally be at the same feature density as that achieved by the BCP. Therefore, Ruiz et al. reported a viable technique based on the use of EBL and oxygen plasma functionalization for cylindrical BCP with pattern density.
multiplication of $2L_0$ (see Figure 3.1.a). Later on, Cheng et al. developed a technique to increase the density multiplication factor of a lamellar PS-$b$-PMMA BCP, based on 193 nm immersion lithography. In 2010, Sanders et al. from IBM presented a chemical epitaxy DSA flow using sparse chemical pre-patterns made by a pattern-first, neutralize-last approach. Based on these works, industry focused BCP DSA as a potential complementary technique for the next generation logic nodes. However, the defect density has to be decreased down to 0.01 defects/cm², and thus, in order to achieve the defectivity level required by the industry, Liu and Nealey in 2011 developed the LiNe process. In this process, two materials with different chemical affinities are employed to create the chemical guiding pre-patterns. As shown in the scheme from Figure 3.1.b, the process flow starts by spin-coating a cross-linkable polystyrene (X-PS) on a substrate and after a lithography step, the material is etched. Then, a random hydroxyl terminated poly(styrene-block-methyl methacrylate) (PS-$r$-PMMA-OH) brush is spin-coated and grafted to the substrate between the X-PS guiding stripes, creating thus a chemical pattern. The X-PS guiding stripes are more affine to PS domains while the PS-$r$-PMMA background stripes have equal affinity for both domains. Other approaches combining the use of topographical and chemical patterns have been also presented by Kim et al. in which the BCP is self-assembled on top of grapho-chemical pre-pattern.

Nowadays, the main research objective for DSA on chemical patterns is to meet the manufacturing requirements of the semiconductor industry (low defectivity, process integration and device design with DSA patterns). Nevertheless, new processes and materials must be developed to demonstrate resolutions up to 5 nm of BCP half-pitch, to serve DSA manufacturing processes able for more than two future node generations. Therefore, for the complete incorporation of DSA processes it is necessary to understand the physics and chemistry that enables the integration of BCPs with traditional manufacturing processes.

In this chapter, the implementation, characterization and modelling of a chemical epitaxy process for PS-$b$-PMMA based on the functionalization of the substrate after an EBL is presented. First, this method has been implemented at laboratory scale, at the IMB-CNIM cleanroom. Then, in order to demonstrate the industrial scalability of the process, it has been transferred to CEA-Leti’s cleanroom, which is more industrial focused and has a compatible pilot line for the fabrication of CMOS integrated circuits.

On the other hand, two other novel chemical epitaxy approaches based on direct writing techniques are presented. These two direct writing techniques are based on using EBL and atomic force microscopy (AFM) directly on the substrate, thus avoiding the use of resist and the corresponding development and stripping steps.
3. Directed self-assembly of PS-b-PMMA block copolymers by chemical epitaxy

![Fig 3.1](image)

**Figure 3.1.** Schematic of the chemical epitaxy process developed by (a) Ruiz et al. using e-beam lithography and O₂ plasma functionalization\(^ {13}\) and by (b) Liu and Nealey using an alternate pattern of two polymers (LiNe process)\(^ {18}\)

3.2. Development and implementation of chemical epitaxy by substrate functionalization

Chemical epitaxy based lithography and substrate functionalization methods are those in which an end-grafted homopolymer or random brush polymer is first deposited on top of the substrate, and then patterned by means of a top-down approach. Then, the defined regions are selectively functionalized to change their chemical affinity. This functionalization can be performed by using either oxygen plasma or UV exposure.

In this section, a chemical epitaxy process defined by EBL and oxygen plasma functionalization is presented. First, the process is defined and optimized at the IMB-CNM cleanroom for three different PS-b-PMMA materials, and then for high-\(\chi\) BCPs (see chapter 5). Since chemical epitaxy processes are mainly driven by the difference on the surface free energy between the substrate and the BCP domains, a new experimental process to determine these interactions is also presented. Then, based on these experimental results, the simulation and modelling of this DSA method is performed.

3.2.1. Materials and methods

3.2.1.1. Description of the chemical epitaxy process

A new technique based on using the EBL and oxygen plasma functionalization has been developed and optimized to promote the alignment of PS-b-PMMA and also high-\(\chi\) BCPs.
The process flow is depicted in Figure 3.2. It consists of following steps: (i) polymer brush grafting on the top of a silicon substrate, (ii) e-beam writing on PMMA resist, (iii) resist development and substrate functionalization by oxygen plasma, (v) resist removal and (vi) BCP spin-coating.

Figure 3.2. Schematic of the chemical epitaxy process based on using EBL and oxygen plasma functionalization

3.2.1.2. Brush and block copolymer materials

Lamellae PS-β-PMMA BCPs with different polymer chain lengths have been used for the DSA process, each one processed with its own polymer brush and annealing conditions in order to fine-tune the interface energies that provide an optimal alignment (see Table 3.1 and Table 3.2 for brush and BCP specifications).

For each BCP, different brush layers based on PS-γ-PMMA and PS-OH and in consequence different processing conditions, have been tested. The brush layer and processing conditions used for each BCP are specified in Table 3.3.

Table 3.1. Specifications of brush layer materials used for chemical epitaxy DSA

<table>
<thead>
<tr>
<th>Material</th>
<th>Molecular weight</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-OH</td>
<td>4.5 kg/mol</td>
<td>1.34</td>
</tr>
<tr>
<td>PSγ=0–β-PMMA</td>
<td>9.9 kg/mol</td>
<td>1.09</td>
</tr>
<tr>
<td>PSγ=0–γ-PMMA</td>
<td>7.9 kg/mol</td>
<td>1.85</td>
</tr>
</tbody>
</table>

Table 3.2. Specifications of PS-β-PMMA BCP used for chemical epitaxy DSA

<table>
<thead>
<tr>
<th>BCP chemical nature</th>
<th>PS-β-PMMA</th>
<th>PS-β-PMMA</th>
<th>PS-β-PMMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDI</td>
<td>1.09</td>
<td>1.12</td>
<td>1.1</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>79 kg/mol</td>
<td>45 kg/mol</td>
<td>42.3 kg/mol</td>
</tr>
<tr>
<td>PS fraction</td>
<td>50%</td>
<td>50%</td>
<td>48%</td>
</tr>
<tr>
<td>Pitch</td>
<td>38 nm</td>
<td>28 nm</td>
<td>22 nm</td>
</tr>
</tbody>
</table>

Table 3.3. Processing conditions used for PS-β-PMMA BCP DSA

<table>
<thead>
<tr>
<th>Brush material</th>
<th>L₀ = 38 nm</th>
<th>L₀ = 28 nm</th>
<th>L₀ = 22 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Processing conditions</td>
<td>260°C for 5 min, N₂ environment</td>
<td>260°C for 5 min, N₂ environment</td>
<td>230°C for 5 min, N₂ environment</td>
</tr>
<tr>
<td>Film thickness</td>
<td>4.6 nm</td>
<td>4.7 nm</td>
<td>8.6 nm</td>
</tr>
<tr>
<td>BCP</td>
<td>L₀</td>
<td>0.9L₀</td>
<td>0.75L₀</td>
</tr>
<tr>
<td>Processing conditions</td>
<td>230°C for 10 min, N₂ environment</td>
<td>200°C for 20 min, O₂ environment</td>
<td>230°C for 10 min, N₂ environment</td>
</tr>
</tbody>
</table>
3.2.1.3. Substrate preparation and creation of the chemical guiding patterns

The starting substrates are 0.9 x 0.9 cm² chips bearing a native silicon oxide layer (100), p-type silicon wafers of 4-40 Ω · cm resistivity. Previously to the grafting process, the sample surface is cleaned and activated by an oxygen plasma for 10 min at 500 W and 50 sccm oxygen flow. Then a 2% PGMEA brush solution is spin-coated at 5000 rpm on the top of the surface and annealed by using the processing conditions depicted in Table 3.3.

Consequently, the non-grafted brush is removed by dipping the sample in PGMEA for 5 min in an ultrasound bath at 40°C. The brush film thickness grafted after PGMEA rinsing depends on brush molecular weight (see Table 3.3). Then, a 2% 950k PMMA solution is spin-coated on the top of the brush at 2000 rpm giving rise to an 80 nm film thickness. Once the resist has been deposited, the guiding patterns are defined by EBL in a RAITH 150Two equipment. Figure 3.3 depicts the definitions regarding guiding pattern dimensions and BCP specifications that are going to be used from now on through the manuscript (d denotes the BCP film thickness, L₀ is the BCP pitch, and L_s and L_b refer to guiding and background stripe widths, respectively). Guiding patterns for line/space applications with guiding stripes widths between 0.5L₀ to 3.5L₀ and density multiplication factors of 2L₀ to 7L₀ have been designed.

The EBL has been performed by exposing the desired patterns at 20 kV and 110 pA of beam current with a nominal beam diameter of 2 nm. The exposure has been defined as a set of single line exposures and e-beam doses between 225 and 675 μC/cm² have been used in order to obtain the desirable line widths. This means that the writing speed has been varied between 4.9 and 1.6 m/s by using a line step size of 10 nm.

![Guiding pattern dimensions and BCP specifications scheme](image)

**Figure 3.3.** Guiding pattern dimensions and BCP specifications scheme

After the exposure, the resist is developed by dipping the sample in a methyl isobutyl ketone (MIIBK) and isopropanol (IPA) solution at 1:3 for 30 s and then, in IPA for a further 30 s. Subsequently, the sample defined areas are exposed to oxygen plasma in order to chemically change their structure.

3.2.1.4. Functionalization of the surface and PS-b-PMMA spin-coating

Once the sample has been developed after the EBL exposure, it is subjected to a brief dose of oxygen plasma in order to chemically change the substrate affinity. It is known that
3. Directed self-assembly of PS-\textit{b}-PMMA block copolymers by chemical epitaxy

Oxygen plasma creates polar groups on the brush creating regions more affine to PMMA (see Figure 6.4.c).\textsuperscript{21}

The functionalization is performed in an \textit{Alcatel AMS 110 DE} reactive ion etching (RIE) equipment by using two different conditions denoted as soft and strong (see specifications in Table 3.4). Two different conditions have been used in order to study how the BCP morphology changes as a function of the interactions between the BCP domains and the different functionalized regions.

<table>
<thead>
<tr>
<th>[O\textsubscript{2}] (sccm)</th>
<th>Soft O\textsubscript{2} plasma</th>
<th>Strong O\textsubscript{2} plasma</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power Source (W)</td>
<td>150</td>
<td>300</td>
</tr>
<tr>
<td>Time (s)</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>Pressure (Pa)</td>
<td>1.33</td>
<td>1.33</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Brush removed</td>
<td>0.6 nm</td>
<td>4.5 nm</td>
</tr>
</tbody>
</table>

After performing the brush functionalization, the resist is removed by dipping the sample into acetone for 2 min in an ultrasound bath at 40°C. Figure 3.4 shows AFM images of the topography and phase signals of a chemical guiding pattern created on a PS-OH brush layer by soft oxygen plasma functionalization after removing the PMMA resist. Brighter and darker areas correspond to the background and guiding stripes, respectively.

The chemical contrast revealed by the AFM phase image is a signature of the fact that the un-exposed PS-OH (background regions) are slightly affine to polystyrene, while the stripes exposed to oxygen plasma are slightly affine to PMMA due to the oxidation of the polymer. Furthermore, it is observed that oxygen plasma exposure induces a removal of around 0.5 nm of PS-OH (Figure 3.4.a).

The presence of some topography between stripes may enhance the guiding efficiency of the chemical patterns, although it is not enough to induce the alignment of the BCP.\textsuperscript{9,25}

Finally, a 1.5\% PGMEA solution of BCP is spin-coated on the top of the chemical guiding pattern and it self-assembles with respect to the previous pattern after a thermal annealing treatment. Processing conditions (brush material, BCP film thickness, annealing temperatures and time) for each BCP are summarized in Table 3.3.
3. Directed self-assembly of PS-b-PMMA block copolymers by chemical epitaxy

![Figure 3.4. AFM topography (a) and phase (b) images of a chemical guiding pattern created by e-beam exposure followed by oxygen plasma modification](image)

3.2.2. Directed self-assembly by chemical epitaxy of PS-b-PMMA results

The PS-b-PMMA DSA process has been studied for three molecular weight systems. First, the results for the 28 nm pitch are presented, and then those for the 38 nm and 22 nm, respectively.

**PS-b-PMMA 28 nm pitch directed self-assembly**

First DSA experiments were performed with PS-b-PMMA of 14 nm half-pitch by varying the multiplication factor and by keeping constant the guiding stripe width at 0.5L_0. Figure 3.5 shows an example of PS-b-PMMA DSA for a guiding stripe width of 0.5L_0 and density multiplication factors of 3L_0 and 4L_0. As it can be observed the BCP is well self-assembled with respect to the previous chemical pattern as a function of the guiding pattern pitch. Furthermore, Figure 3.6 shows that the process is transferable to larger guiding patterns showing low defectivity.

On the other hand, when the guiding pattern dimensions are not in registry with the BCP pitch, the alignment is lost all along the guiding pattern (Figure 3.7). For this later example, guiding and background stripe widths are 0.5 and 4L_0, respectively, and because the background stripe width does not fit with (0.5+n)·L_0, the accurate BCP alignment is not achieved.

Nevertheless, despite being an appropriate method to guide this 28 nm pitch BCP, the required resolution of the beam is 14 nm since the guiding stripe dimensions are set to be the half of the BCP pitch. Therefore, the method is somehow disadvantageous due to the fact that it introduces a lithographic step, nominally at the same feature density as that achieved by the BCP.
3. Directed self-assembly of PS-b-PMMA block copolymers by chemical epitaxy

![Image](image_url)

**Figure 3.5.** PS-b-PMMA (L₀ = 28 nm) DSA for Lₚ = 0.5L₀ and density multiplication factors of (a) 3L₀ and (b) 4L₀

![Image](image_url)

**Figure 3.6.** PS-b-PMMA (L₀ = 28 nm) DSA in a large area for Lₚ = 0.5L₀ and density multiplication factor of 3L₀

![Image](image_url)

**Figure 3.7.** PS-b-PMMA (L₀ = 28 nm) DSA for Lₚ = 0.5L₀ and L₀ = 4L₀ showing no BCP alignment due to the non-commensurability of the pattern with the BCP pitch

As a solution, guiding patterns with wider guiding stripes have been designed in order to relax the lithography resolution requirements and extend the implementation of the process.
for the next generation BCP materials with smaller pitch. Figure 3.8 illustrates the density multiplication concept when using $0.5L_0$ or $(0.5+n) \cdot L_0$ guiding stripe widths. The concept behind this approach is that by properly tuning the brush functionalization, when using wide guiding stripes, more than one standing perpendicular lamellae is located on top of guiding stripes, thus avoiding lying lamellae.

To experimentally demonstrate the effect of the brush functionalization on the BCP alignment, guiding patterns with the same dimensions have been exposed to two different oxygen plasma conditions (referred to soft and strong), depicted previously in Table 3.4, and using the same BCP material. As shown in Figure 3.9.a, when soft oxygen plasma conditions are used slightly PMMA affine regions can be obtained, favoring standing perpendicular lamellae. In that situation, $3.5L_0$ wide guiding stripes were exposed and thus, four PMMA and three PS stripes are on top of them. On the other hand, the non-exposed regions ($1.5L_0$) which are slightly affine to PS, have three PS and two PMMA stripes. When stronger conditions are used, lying lamellae is promoted due to the strong surface affinity for PMMA, as shown in Figure 3.9.b. Based on these DSA results, it can be concluded that by properly tuning the oxygen plasma conditions, the BCP wetting behavior can be accurately controlled, enabling the possibility of achieving and controlling different alignment morphologies.

![Image](image.jpg)

**Figure 3.8.** DSA by chemical epitaxy schemes showing the concept of density multiplication. $L_s$ denotes the width of the chemical guiding stripes, and $L_0$ represents the separation between guiding stripes (background). The density multiplication factor is defined as the ratio between the period of the guiding pattern and that of the BCP.

![Image](image.jpg)

**Figure 3.9.** PS-PMMA ($L_0 = 28$ nm) DSA when using (a) soft and (b) strong plasma conditions. Red and green colors refer to soft and strong functionalization, respectively, while blue color depicts background regions.
**PS-b-PMMA 38 and 22 nm pitch directed self-assembly**

To demonstrate that the process is scalable to other BCP polymer chain lengths, two additional BCPs with 38 nm and 22 nm pitch have been used with a guiding and background stripe widths of 0.5L₀ and 1.5L₀, respectively (material specifications and processing conditions are depicted in Table 3.1, Table 3.2 and Table 3.3, respectively).

As shown in the SEM images from Figure 3.10, the BCP has been aligned by following the chemical pre-pattern, although different processing conditions have had to be used for each BCP. This is attributed to the fact that depending on the BCP molecular weight the interactions taking place between the domains and the surface are different. This effect will be later on studied by the experimental characterization of surface free energies.

Moreover, the DSA method has been also tried for guiding patterns with wider guiding stripes, but it has not been successful for the case of 38 nm pitch PS-b-PMMA, as it has been for the case of 22 nm pitch demonstrated in Figure 3.11. In this later situation, guiding stripe widths of 1.5L₀ have kept constant while the guiding pattern pitch has been varied up to density multiplication factors of 5L₀. Above 5L₀ pitch, fingerprint morphology is started to be seen in between background regions because the chemical pattern is not strong enough to drive the BCP alignment.

![Figure 3.10](image1.png)  
**Figure 3.10.** PS-b-PMMA DSA when using 0.5L₀ width guiding stripes and density multiplication factor of 2L₀ for BCP pitch of (a) 38 nm and (b) 22 nm

![Figure 3.11](image2.png)  
**Figure 3.11.** PS-b-PMMA (L₀ = 22 nm) DSA for Lₙ = 1.5L₀ and density multiplication factors of (a) 3L₀ (b) 4L₀ and (c) 5L₀. Red color refers to guiding stripes width (Lₙ = 1.5L₀)

On the other hand, it is known that BCP morphology strongly depends on the BCP film thickness. In order to find out the optimal film thickness which provides the best DSA results, a range of different thicknesses has been studied for each BCP. As an example of it,
Figure 3.12 shows SEM images of PS-\(b\)-PMMA (\(L_0 = 38\) nm) on top of the same chemical guiding pattern (\(L_s = 0.5L_0\) and \(L_b = 1.5L_0\)) by using different values of film thickness. It is clearly observed that the morphology and phase separation behavior strongly depends on the BCP film thickness. For this BCP, the best result is obtained when the film thickness is \(0.9L_0\).

![Figure 3.12. PS-\(b\)-PMMA (\(L_0 = 38\) nm) DSA for \(L_s = 1.5L_0\) and density multiplication factor of 2\(L_0\) with film thickness values of (a) 0.8\(L_0\), (b) 0.9\(L_0\), (c) 0.96\(L_0\) and (d) 1.1 \(L_0\)](image)

In short, it has been demonstrated that the DSA of PS-\(b\)-PMMA by chemical epitaxy with O2 plasma functionalization has been successfully implemented with different BCP chain lengths and high density multiplication factors, although the largest pitch BCP has not been possible to align by using wide guiding stripes patterns and high density multiplication factors. This may be attributed to the high interaction that exists between the stripes and the domains of the BCP.

In order to understand how the BCP behaves at the bottom of the guiding pattern and thus check which interactions are taking place between the blocks and the chemical pattern, a cross-section SEM image, after selectively removing the PMMA domains by an oxygen plasma has been taken.

From Figure 3.13 it can be gathered that PS domains slightly wet the PS-OH brush layer in non-modified regions (brown stripes). That means that the interaction between the brush and the PS domains is too strong to ensure the perpendicular BCP morphology from the top to the bottom, promoting a PS wetting layer at the bottom of the guiding pattern. Therefore, it is difficult to direct self-assemble the BCP through the entire guiding pattern with higher density multiplication factors.

On the other hand, to avoid this wetting behavior on background regions different random copolymer brush layers (PS-\(\pi\)-PMMA) with PS contents between 0.6 and 1 have been tried for different processing conditions. Nevertheless, there has not found an optimal alignment condition for any of the brush layers used.
3. Directed self-assembly of PS-b-PMMA block copolymers by chemical epitaxy

![SEM cross-section of PS-b-PMMA (L₀ = 38 nm) DSA for L₀ = 0.5L₀ and density multiplication factor of 2L₀](image)

**Figure 3.13.** SEM cross-section of PS-b-PMMA (L₀ = 38 nm) DSA for L₀ = 0.5L₀ and density multiplication factor of 2L₀

3.3. Characterization of the surface free energy of chemical guiding patterns

As discussed in previous chapters, the self-assembly of BCPs oddly leads to perfect structures without defects. Sometimes the system is kinetically trapped into a metastable morphology. Therefore, computer simulations are used to optimize the self-assembly process on the guiding patterns by using SCFT or Ginzburg-Landau theory (TDGL) of the Ohta-Kawasaki model.

In chemical epitaxy DSA, the achievement of the proper BCP alignment with high density multiplication factors depends on the chemical pattern dimensions and on the interface energies between the guiding features and the BCP domains. By controlling the interactions between the substrate and the BCP domains together with an accurate guiding pattern design, large aligned BCP areas have been experimentally demonstrated.

3.3.1. Experimental method to determine the interface interactions for modeling the chemical epitaxy DSA process

3.3.1.1. Materials and methods

*Description of the overall process to determine the surface free energy*

The difference of surface free energy between homopolymers A and B, can be experimentally determined by performing homopolymer blend dewetting experiments.

This novel approach, depicted in Figure 3.14, allows measuring the contact angle between homopolymers in a polymer blend, and thus calculating the difference on the surface free energy. First, a 50:50 A:B homopolymer blend is spin-coated on the top of a brush layer (un-modified and chemically modified), and it is subsequently annealed under the same conditions than those for which BCP is optimally aligned.
After the annealing, if the substrate is not attractive enough to both homopolymers, a set of droplets is obtained. In most of the cases, the homopolymer blend layer dewetts, forming a drop-in-drop structure which contains both homopolymers.

As it can be seen in more detail in the cross-section of Figure 3.14, the droplets are generally formed by one polymer droplet surrounded by the other polymer. Then, one of the two domains is selectively removed and the contact angle is characterized by SEM cross-section imaging.

![Figure 3.14. Overall fabrication process to determines the contact angle between homopolymers](image)

The contact angle between homopolymer determines the surface affinity for both BCP domains. If $\Phi_{A:B} < 90^\circ$, then the surface is more affine to B and if $\Phi_{A:B} = 90^\circ$, then the surface presents equal affinity for both homopolymers.

**Polymer brush and processing conditions**

In order to find out the interactions taking place at the surface in the different chemical epitaxy processes described in section 3.2, PS/PMMA contact angle experiments are carried out. Different brush layer materials and BCP and surface processing conditions (non-modified and chemically modified surfaces by using soft and strong oxygen plasma conditions) have been used.

The systems chosen to characterize the surface free energies have been those in which the different BCPs have shown an optimal DSA behavior (Table 3.5). The optimal DSA conditions have been selected according with the experiment results shown in the previous section.

The performed experiments are detailed in Table 3.6. These experiments have been selected in accordance to brush material/annealing and BCP. Then for each optimized DSA system (pair of brush/annealing and BCP), modified and un-modified surfaces have been characterized (three first rows of Table 3.6). Additionally, to compare the DSA results, two other systems in which none of BCPs has shown DSA, have been analyzed (two last rows of Table 3.6).
Table 3.5. Optimal DSA processing conditions obtained for PS-<i>b</i>-PMMA of 38, 28 and 22 nm pitch

<table>
<thead>
<tr>
<th>Block copolymer</th>
<th>Brush layer + annealing</th>
<th>BCP annealing</th>
<th>SEM image</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-&lt;i&gt;b&lt;/i&gt;-PMMA</td>
<td>PS-OH 260°C, 5 min in N₂</td>
<td>230°C, 10 min in N₂</td>
<td>![SEM image]</td>
</tr>
<tr>
<td>L₀ = 38 nm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS-&lt;i&gt;b&lt;/i&gt;-PMMA</td>
<td>PS-OH 260°C, 5 min in N₂</td>
<td>200°C, 20 min in hot-plate</td>
<td>![SEM image]</td>
</tr>
<tr>
<td>L₀ = 28 nm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS-&lt;i&gt;b&lt;/i&gt;-PMMA</td>
<td>PS₁₀₀₋ᵣ-PMMÁ 230°C, 5 min in N₂</td>
<td>230°C, 10 min in N₂</td>
<td>![SEM image]</td>
</tr>
<tr>
<td>L₀ = 22 nm</td>
<td></td>
<td></td>
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</tbody>
</table>

Table 3.6. PS/PMMA contact angle experiments performed, describing the processing conditions (brush layer and BCP processing)

<table>
<thead>
<tr>
<th>Brush + annealing</th>
<th>PS/PMMA annealing</th>
<th>Chemical functionalization</th>
<th>BCP DSA</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>PS-OH 260°C, 5 min in N₂</td>
<td>200°C, 20 min in hot-plate</td>
<td>Non-modified</td>
</tr>
<tr>
<td>B</td>
<td>PS-OH 260°C, 5 min in N₂</td>
<td>200°C, 20 min in hot-plate</td>
<td>Modified with soft O₂ conditions</td>
</tr>
<tr>
<td>C</td>
<td>PS₁₀₀₋ᵣ-PMMÁ 230°C, 5 min in N₂</td>
<td>230°C, 10 min in N₂</td>
<td>Modified with strong O₂ conditions</td>
</tr>
<tr>
<td>D</td>
<td>PS₁₀₀₋ᵣ-PMMÁ 230°C, 5 min in N₂</td>
<td>230°C, 10 min in N₂</td>
<td>Not achieved</td>
</tr>
<tr>
<td>E</td>
<td>PS₁₀₀₋ᵣ-PMMÁ 230°C, 5 min in N₂</td>
<td>230°C, 10 min in N₂</td>
<td></td>
</tr>
</tbody>
</table>

3.3.1.2. Experimental determination of surface free energy

After PS/PMMA spin-coating and annealing, PMMA domains are selectively removed by oxygen plasma in order to characterize the samples by SEM cross-section imaging. Figure 3.15 shows a schematic representation of the drop-in-drop structure that the homopolymer blend takes after the annealing in both un-modified and modified surfaces. Figure 3.15.a represents a surface slightly more attractive to A domains (red), whereas Figure 3.15.b strongly to B (blue). The wetting behavior is not strong in Figure 3.15.a and therefore there is no polymer wetting layer, as there is in Figure 3.15.b where the surface is strongly B affine.
SEM images of PS/PMMA polymer blend droplets on top of un-modified and modified (soft) PS-OH brush layers after removing PMMA domains are shown in Figure 3.16 (SEM images correspond to the PS/PMMA experiment depicted in the first row of Table 3.17). From Figure 3.16.a it can be observed that the measured contact angle between PS and PMMA is 60.6° indicating a more PS affine surface. On the contrary, when the surface is functionalized by oxygen plasma exposure, the chemical affinity becomes more PMMA attractive, as revealed by the contact angle value of 140.5°.

The behavior of the polymer blend not only depends on the substrate functionalization (depicted in Figure 3.15), but also on the brush chemistry. Figure 3.17 shows SEM images of PS/PMMA homopolymer blend on top of different brush layer materials. It can be observed, that the higher the content of PMMA in the brush, the higher the value of the contact angle due to the increase of PMMA affinity.
From the contact angle between homopolymers, the difference on the surface free energy is determined by the Young’s Equation

\[ \gamma_S = \gamma_{SL} + \gamma_L \cdot \cos \theta, \]  

(3.1)

where \( \gamma_S \) and \( \gamma_L \), represent the surface free energy of the surface and the liquid, respectively, \( \gamma_{SL} \) is the surface tension between the surface and the liquid, and \( \theta \) is the contact angle between the liquid and the surface.

For homopolymer blends, equation (3.1) becomes:

\[ \gamma_{A-\text{Surface}} - \gamma_{B-\text{Surface}} = \gamma_{AB} + \gamma_L \cdot \cos \theta_{AB}, \]  

(3.2)

where \( \gamma_{A-\text{surface}} \) and \( \gamma_{B-\text{surface}} \) are the interface tensions between homopolymers, and \( \gamma_{AB} \) is the surface free-energy between A and B which depends on the annealing temperature and can be obtained from the literature. The interfacial tension between PS and PMMA as a function of the annealing temperature reported in the literature is (3.3)\textsuperscript{28}

\[ \gamma_{\text{PS/PMMA}} \text{ [mN/m]} = 3.6 - 0.013T \text{ [°C]}, \]  

(3.3)

For each system described in Table 3.6 and by using equations (3.2) and (3.3), the difference on the surface free energy is calculated. Table 3.7 and Table 3.9 show the values of the experimental interface energies obtained from the contact angle measurements.

**Table 3.7.** Values of experimental interface energies obtained from contact angle measurements and the corresponding alignment results achieved after the optimal DSA process (A, B, C).

<table>
<thead>
<tr>
<th>System</th>
<th>A (PS-OH(_b))</th>
<th>B (PS-OH(_a))</th>
<th>C (PS(<em>{\text{SO}</em>{3}^{-}})-PMMA)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Un-modified</td>
<td>Soft O(_3) plasma</td>
<td>Strong O(_3) plasma</td>
</tr>
<tr>
<td>( \Phi )</td>
<td>60.6°</td>
<td>140.5°</td>
<td>156.6°</td>
</tr>
<tr>
<td>( \cos \Phi )</td>
<td>0.49</td>
<td>-0.77</td>
<td>-0.91</td>
</tr>
<tr>
<td>( \gamma_{\text{PS/PMMA}} )</td>
<td>1 mN/m</td>
<td>0.61 mN/m</td>
<td></td>
</tr>
<tr>
<td>( \gamma_{\text{PMMA/Brush}} - \gamma_{\text{PS/Brush}} )</td>
<td>0.49 mN/m</td>
<td>-0.77 mN/m</td>
<td>-0.92 mN/m</td>
</tr>
</tbody>
</table>
Table 3.8. Values of experimental interface energies obtained from contact angle measurements of two polymer brush (D, E)

<table>
<thead>
<tr>
<th>System</th>
<th>D (PS95/r-PMMA)</th>
<th>E (PS95/r-PMMA)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Un-modified</td>
<td>Soft O₂ plasma</td>
</tr>
<tr>
<td>Φ</td>
<td>107.7°</td>
<td>154.5°</td>
</tr>
<tr>
<td>COS Φ</td>
<td>-0.30</td>
<td>-0.90</td>
</tr>
<tr>
<td>γ&lt;sub&gt;PS/PMMA&lt;/sub&gt;</td>
<td>0.61 mN/m</td>
<td></td>
</tr>
<tr>
<td>γ&lt;sub&gt;PMMA-Brush&lt;/sub&gt; - γ&lt;sub&gt;PS-Brush&lt;/sub&gt;</td>
<td>-0.19 mN/m</td>
<td>-0.55 mN/m</td>
</tr>
</tbody>
</table>

From the values of Table 3.7 it can be observed that for the systems A, B and C, the surface is PS affine in the background regions, and this affinity is higher as the PS content of the brush is larger. On the other hand, after the functionalization, the guiding stripes become more PMMA affine. It can be observed that this interaction is higher when the oxygen conditions are stronger.

Comparing the oxygen plasma treatments, the different value of γ<sub>PMMA-Brush</sub> - γ<sub>PS-Brush</sub> explains the different morphologies that the BCP takes depending on the chemical guiding pattern strength (Figure 3.9 and system A depicted in Table 3.7). When the guiding stripes are created by soft oxygen plasma, they are slightly affine to PMMA domains γ<sub>PMMA-Brush</sub> - γ<sub>PS-Brush</sub> = -0.77 mN/m, promoting not a strong but a slight interaction with the guiding pattern, and forming perpendicular lamellae. In turn, when using strong oxygen plasma, the guiding stripes become strongly affine to PMMA γ<sub>PMMA-Brush</sub> - γ<sub>PS-Brush</sub> = -0.92 mN/m, favoring laying lamellae. On the other hand, as discussed before, background stripes present slightly affinity to PS domains γ<sub>PMMA-Brush</sub> - γ<sub>PS-Brush</sub> = 0.49 mN/m. Moreover, by comparing B to E systems (different brush, and same BCP processing conditions), it can be observed that the higher the content on PS in the brush the higher is the difference on the surface free energies.

From the characterization of the surface free energies, it can be first concluded that the surfaces becomes more PMMA attractive after the functionalization of the brush, but the chemical interaction that takes place strongly depends on the conditions used. Therefore, by properly tuning these modifications on the substrate, an optimal set of interface energies which provides a DSA with very low defectively can be found. It has been demonstrated that for each block copolymer, the optimal set of interface energies is determined by the brush layer material and its processing conditions, and by the block copolymer annealing.

On the other hand, it is also important to remark that in order to have a good alignment by chemical epitaxy, background areas need to be slightly affine to the contrary domain the guiding regions are. This is demonstrated when using PS95/r-PMMA brush (depicted by system D in Table 3.8), in which the DSA is lost since both regions (modified and un-modified) are PMMA attractive.
Figure 3.18 shows a graph illustrating the difference of surface free energy ($\gamma_{PMMA-Brush} - \gamma_{PS-Brush}$) on background (pink) and guiding (blue and green) regions, as a function of the brush PMMA content. When the same BCP processing conditions are used (systems B to E), it is observed that the higher the PMMA content on the brush layer, the lower is the difference on the $\gamma_{PMMA-Brush} - \gamma_{PS-Brush}$, between soft and strong functionalization. This occurs because the higher the PMMA content on the brush, the less PS molecules, the oxygen has to react with. On the other hand, for this situation, it can also be drawn that the lower the PMMA content, the higher is the difference between modified and un-modified regions, being this situation more suitable for higher molecular weight BCP (system B).

On the other hand, it is seen that the final DSA behavior strongly depends on the BCP annealing. It is reflected in systems A and B, in which the same brush conditions are used, but the BCP annealing conditions are different. This happens because the interfacial energy between PS and PMMA depends on the BCP annealing (equation (3.3)), and it is higher when the BCP annealing temperature decreases. This increase in the interfacial energy between PS and PMMA, makes the system have a larger difference between guiding and background surface free energies.

Figure 3.18. Representation of the difference free energy ($\gamma_{PMMA-Brush} - \gamma_{PS-Brush}$) on background (pink) and guiding (blue and green) regions, as a function of the brush PMMA content. SEM images correspond to the optimal DSA results obtained for each BCP pitch (systems A, B and C).

To demonstrate that a specific BCP system requires a particular set of interface energies, each BCP has been processed by using the optimal alignment conditions of the other two BCPs. Figure 3.19, shows SEM images of each BCP (38 nm, 28 nm and 22 nm pitch) aligned by using the conditions A, B and C. It can be observed from the results, that each BCP only gets an optimal DSA under specific processing conditions, and it becomes disordered when either the brush or the BCP annealing conditions are changed.
3. Directed self-assembly of PS-b-PMMA block copolymers by chemical epitaxy

![Image of BCP DSA results comparison](image)

**Figure 3.19.** Comparison of the BCP DSA results obtained for the three optimal set of interface energies found (A, B and C). \( \Delta \gamma_{bs} \) and \( \Delta \gamma_{ss} \), denote the difference of surface free energy on background and guiding stripes, respectively.

3.3.2. Role of the surface interactions by field-theoretic simulations and self-consistent field theory on chemical epitaxy DSA process

The chemoepitaxy process has been modeled by using a soft coarse grained model, as described previously in section 2.3. Single-Chain-in-Mean-Field (SCFM) simulations of the soft, coarse-grained model have been carried out to study the BCP structure formation on chemical patterned substrates. Additionally, self-consistent calculations have been used to compute the free-energy and the thermodynamic forces that drive the structure formation. This work has been performed in collaboration with Marcus Müller group (*Computational Soft Condensed Matter*) at the Georg-August-Universität of Göttingen.

The achievement of high density multiplication factors on DSA chemical epitaxy processes, requires considering multiple parameters. The most relevant ones are of dimensional nature, material and process related, all of them depicted in Table 3.9. While most of these parameters are known either because they are unequivocally experimentally determined, from the literature or from modelling/simulation, the surface free-energies are sensitively dependent on the experimental conditions, and the accurate quantitative estimation of their values has almost not been addressed up to now. Furthermore, it has been reported that the main driving force of the chemical epitaxy process is the difference on the surface-free energy of BCP domains with the confining boundaries, and therefore it is very important to
3. Directed self-assembly of PS-b-PMMA block copolymers by chemical epitaxy

determine them. In order to run simulations and model the chemical epitaxy DSA process, surface free energy experimental data reported in the previous section, has been introduced into the DSA model.

**Table 3.9.** Description of the pattern dimensions and invariant parameters of the coarse-grained model

<table>
<thead>
<tr>
<th>Dimensional parameters</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_g$</td>
<td>Width of guiding stripe</td>
</tr>
<tr>
<td>$L_b$</td>
<td>Width of background stripe</td>
</tr>
<tr>
<td>$L_0$</td>
<td>Bulk lamellae period</td>
</tr>
<tr>
<td>$d$</td>
<td>BCP film thickness</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Material parameters</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi_N$</td>
<td>Flory Huggins parameter · degree of polymerization</td>
</tr>
<tr>
<td>$R_{cc}$</td>
<td>Mean square end-to-end BCP chains distance</td>
</tr>
<tr>
<td>$\kappa N$</td>
<td>Inverse isothermal compressibility of the liquids · degree of polymerization</td>
</tr>
<tr>
<td>$D$</td>
<td>Self-diffusion coefficient</td>
</tr>
<tr>
<td>$\gamma_{SA}$, $\gamma_{SB}$</td>
<td>Surface free-energies of the segments species with the confining boundaries</td>
</tr>
</tbody>
</table>

The molecular connectivity of the chain molecules is described by discretized Edwards Hamiltonian, and the non-bonded interactions are modeled by a local free-energy function that depends on the local density of A and B beads. The confining surfaces at the top and bottom of the film are represented by impenetrable walls where the top wall is neutral and the bottom wall has a chemical stripe pattern that symmetrically attracts one segment species and repels the other. An incompressible melt of symmetric AB diblock copolymers confined between a neutral surface and a bottom surface with a chemical guiding pattern is studied in the simulations.

In the soft, coarse-grained model, the strength of the affinity for wetting is characterized by the parameter $\Lambda N$. Assuming a trivial density profile at the confining surface, Young’s equation yields the following prediction in the strong segregation limit (SSL):

$$\cos(\Theta_{AB}) = \frac{\Delta Y}{\gamma_{AB}} = \frac{12\pi}{\chi_N} \left(1 - \frac{4\ln 2}{\chi_N}\right)^{-1} \cdot \Lambda N = c \cdot \Lambda N,$$

(3.4)

By this way, the interactions between the blocks and the surface are determined by two parameters, $\Lambda N$ and $\Lambda_0 N$, quantifying the preference of the guiding and background stripes, respectively. By knowing these values, it can be easily determined which will be the BCP domains behavior with respect to the modified and un-modified regions. To validate the linear relation between the cosine of the contact angle and the surface preference, and thus accurately determine the constant of proportionality, $c$, as a function of incompatibility and chain length, simulations have been performed. Then, the relation between the contact angle and the strength of the surface affinity for a symmetric homopolymer blend can be mapped.
The simulated system is defined by the parameters depicted in Table 3.10 with linear assignment between particle positions and grid points, hard walls on top and bottom, and antisymmetric surface fields of strength $\Lambda N$, i.e. $\Lambda_0 N = -\Lambda_1 N$. The antisymmetric set-up gives rise to a nearly straight AB interface that runs from the bottom to the top surface. The minimization of interface curvature allows to accurately measuring the contact angle between the AB interface and the surface. In contrast to a macroscopic droplet set-up, the line tension does not influence the contact angle and the AB interface is not curved.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>32</td>
</tr>
<tr>
<td>$\chi N$</td>
<td>16, 20 and 30</td>
</tr>
<tr>
<td>$\sqrt{N} = \frac{n R_{ee}^3}{V}$</td>
<td>90 and 128</td>
</tr>
<tr>
<td>$V$</td>
<td>$2.56 \times 10^2 B_{ee}^3$</td>
</tr>
</tbody>
</table>

Table 3.10. Simulation system parameters

Figure 3.20 presents the $\cos (\phi_{AB})$ as a function of the strength of the surface interaction $\Lambda N$, as obtained from the simulation data compared with the analytical prediction (dashed lines). Simple linear fits (solid lines) yield $\cos (\phi_{AB}) = c \cdot \Lambda N$ with $c = 1.58$ (green), 1.4 (red) and 1.15 (black). Deviations from the analytical prediction arise from discretization effects of the chain contour and space, and from the fact that the analytical formula is obtained in the SSL. Figure 3.21 shows an example of the simulation results for obtaining the relation between the contact angle and surface strength.

Figure 3.20. Relationship between contact angle and surface strength from the analytical prediction (dashed lines) and from simulations. Green, red and black colors represent the values of $\chi N$ 16 ($c = 1.58$), 20 ($c = 1.4$) and 30 ($c = 1.15$), respectively.

Figure 3.21. Examples of simulation of symmetric homopolymer blends for two values of $\chi N$ as a function of the surface strength.
The comparison of the experimental DSA process and simulations has been performed for PS-b-PMMA 22 nm when using wide guiding stripes ($L_w=1.5L_0$ and $L_o=1.5L_0$) and soft oxygen plasma conditions. The experimental DSA result is shown in Figure 3.22, and the values of difference in surface free energy used are summarized in system C of Table 3.7.

![Figure 3.22](image)

**Figure 3.22.** PS-b-PMMA ($L_o=22$ nm) DSA for $L_w$ and $L_o=1.5L_0$. Red and blue stripes denote guiding and background stripes, respectively.

To carry out the simulations, it has to be established a process window where the guiding pattern is strong enough to direct the structure but weak enough to not result in parallel lamellae. However, first simulation results showed that by using the experimental strength values, the guiding pattern was too strong and it gave rise to lying lamellae. This was attributed to the fact that the brush layer is not only characterized by the contact angle, but also for its responsiveness. That is, that there is an interdigitation between the brush and BCP before the structure formation.

Figure 3.23 shows a graph representing the relation between the contact angle and the brush composition (%PMMA) for different brush grafting densities. Black, blue and red color lines represent a high ($h=0.7R_{c\alpha}$), intermediate ($h=0.5R_{c\alpha}$) and low ($h=0.35R_{c\alpha}$) grafting density, whereas the dashed and solid blue lines limit the process window with the contact angle values of guiding and background regions, respectively. The simulations have been carried out for a system with $L_o=1.67R_{c\alpha}$, $\chi N=17$ and $D=\%L_o$. From the graph, it can be observed that intermediate grafting density is closer to experimental results.

![Figure 3.23](image)

**Figure 3.23.** Relation between contact angle and brush composition for different brush grafting densities (black, blue and red colors refer to high, intermediate and low grafting density, respectively, and dashed and solid blue lines represent the cos ($\phi_{bg}$) of background and guiding stripes)
Figure 3.24 show the SCMF simulation results as a function of the brush grafting density. As discussed previously, standing lamellae are favored when the brush thickness is decreased.

![Figure 3.24. SCMF simulation results for a thin BCP film and using (a) high, (b) intermediate and (c) low grafting density](image)

In conclusion, a model has been introduced which validates the DSA chemical epitaxy process when wide guiding stripes are used. Experimental values of surface free energies, determined by using a novel approach, are introduced on the DSA model to run the simulations. From the results obtained, it has been observed that the role of the interfacial free energy is not only the key parameter for the simulation, but also the brush responsiveness.

3.4. Manufacturability of chemical epitaxy by substrate functionalization

As a further step towards, the industrialization chemical epitaxy process developed at IMB-CNMM (CSIC) for PS-b-PMMA systems has been transferred to CEA-Leti (Grenoble, France).

CEA-Leti is a Laboratory for Electronics and Information Technology which is operated by the Direction de la Recherche Technologique at CEA. It mainly aims at helping companies to increase their competitiveness through technological innovation and transfer of its technical know-how to industry. CEA-Leti benefits from 8000 m² cleanrooms in which are working not only people employed by CEA but also co-workers from different industrial companies within the framework of bilateral collaborations. These straight collaborations with industry partners together with the extensive experience on the DSA lithography, makes CEA-Leti a suitable place to study the implementation and manufacturability of the chemical epitaxy process developed at IMB-CNMM to a CMOS compatible 300 mm process line.
3.4.1. Materials and methods

3.4.1.1. Description of the chemical epitaxy process

The overall chemical epitaxy process described in Figure 3.2 has been transferred to CEA-Leti’s pilot line with slight modifications in order to make the process CMOS compatible. Figure 3.25 shows the overall process implemented at Leti’s Pilot line in a SOKUDO DUO lithography track. It consists of 6 steps and except from the EBL and functionalization steps, all the rest have been performed in the same lithography track (SiARC-SOC layers spin-coating, brush grafting, resist development and stripping, and BCP spin-coating and annealing).

It can be noted that the main differences between this process and the one implemented at IMB-CNMM, are the use of CMOS compatible materials, CMOS compatible e-beam positive resist and standard stack for lithography (SiARC-30 nm/SOC-95 nm).

![Figure 3.25. Schematic of the chemical epitaxy process based on using EBL and oxygen plasma functionalization implemented at Leti’s pilot line](image)

3.4.1.2. Brush and block copolymer materials

To study the DSA process and make it to be as similar as possible to the already implemented at IMB-CNMM, the same brush and BCP materials have been used (Table 3.1 and Table 3.2). Nevertheless, the PS-OH brush layer was not available at CEA-Leti, and therefore another hPS (homopolymer polystyrene) brush with different specifications had to be used (molecular weight of 12 kg/mol and PDI of 1.2). As a consequence of having higher molecular weight, the film thickness after removing the non-grafted material results in 5.6 nm.

Regarding BCP materials, PS-\(b\)-PMMA of 38 nm and 22 nm pitch BCPs with the same specifications as the ones used at IMB-CNMM (Table 3.2) have been used. Since PS-\(b\)-PMMA of 28 nm pitch was not available, there has been used a BCP blend (40:60) of 38 nm and 22 nm pitch BCPs.

On the other hand, because the different processing steps involve the use of different solvents, equipment and processing conditions, all the surface free energies have been characterized for different brush layer materials to accurately transfer the DSA process.
3.4.1.3. Substrate preparation and creation of the chemical guiding patterns

The starting substrates are 300 mm silicon wafers (\{100\}, p-type). Previously to the grafting process, 30 nm silicon-containing antireflection coating (SiARC) and 95 nm spin-on carbon (SOC) layers are spin-coated onto the silicon. The coatings are from JSRmicro under the trademark of ISX and HM series, respectively.

The use of these layers has been widely used for advanced semiconductor manufacturing since the 45 nm node.\textsuperscript{29} SiARC and SOC layers work as bottom anti-reflection layers for the photoresist during exposure and the combination of both of them offers a higher reflection control and etch selectivity.\textsuperscript{30} The total reflectivity at the interface must be controlled to be as small as possible in order to have a good critical dimension (CD) control. On the other hand, the thickness of the layers is determined depending on the desired optical and etch requirements. Regarding the etching, fluorine plasma is used to transfer the resist pattern into the SiARC, and then transferred to SOC by oxygen plasma etching.

After the preparation of the substrates, a 2% PGMEA solution of brush is spin-coated at 1500 rpm, annealed at 230°C for 10 min and rinsed away by PGMEA in the same step-process in the track. After rinsing the brush with PGMEA, 50 nm of a compatible CMOS resist (EP555), is deposited on the top of SiArc/SOC substrates and annealed at 130°C. It is important to highlight, that this is a chemically amplified resist (CAR) which enhances the efficiency of e-beam exposure, and thus reduce the effective dose. Then the guiding patterns are defined by using a Vistec SB3054DWBL tool with an energy of 5 keV and e-beam dose of 156 μC/cm². After the e-beam exposure, a resist post-bake is performed at 110°C. The guiding patterns have been designed in order to study different multiplication factors and by using wide guiding stripes for the different BCP dimensions. Figure 3.26 shows a schematic representation of the designed guiding patterns, consisting of arrays of thirty lines by varying the \( L_a \) and \( L_b \) from 20 to 125 nm with steps of 5 nm, in column and row, respectively.

![Schematic representation of the guiding patterns](image)

**Figure 3.26.** Schematic representation of the guiding patterns by varying \( L_a \) and \( L_b \).
3.4.1.4 Functionalization of the surface and PS-b-PMMA spin-coating

The functionalization conditions used at IMB-CNMI have not been possible to implement, because the 300 mm RIE tool available at Leti does not allow the use of very low oxygen flows. Therefore, two of the lowest conditions available for the 300 mm tool have been studied in an inductive (ICP) LAM VERSYS tool (Table 3.11).

Table 3.11. Oxygen plasma conditions for brush functionalization used at CEA-Leti

<table>
<thead>
<tr>
<th>Conditions A</th>
<th>Conditions B</th>
</tr>
</thead>
<tbody>
<tr>
<td>[O₂] (sccm)</td>
<td>100</td>
</tr>
<tr>
<td>Power Source (W)</td>
<td>200</td>
</tr>
<tr>
<td>Time (s)</td>
<td>5</td>
</tr>
<tr>
<td>Pressure (Pa)</td>
<td>1.33</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>20</td>
</tr>
</tbody>
</table>

To determine the interactions of the chemical guiding pattern, a surface characterization has been performed on different modified and non-modified brush materials by analyzing their surface free energy. This characterization has been experimentally carried out by contact angle measurements with the sessile drop method. The Young’s equation (3.1) describes the balance of the three phase contact of a solid-liquid and gas as:

\[ \gamma_{SL} = \gamma_S + \gamma_L - 2\sqrt{(\gamma_L^D \cdot \gamma_S^D) - 2\sqrt{(\gamma_L^P \cdot \gamma_S^P)}} \]

To determine the surface free energy from the contact angle, there are multiple models developed by various researchers. The Owens, Wendt, Rabel and Kaelble theory (OWRK) shows a standard method for calculating the surface free energy of a solid from the contact angle with several liquids. This theory assumes that surface free energy is a sum of independent components, associated with the different interactions (dispersion and polar) that take place:

\[ \gamma_{SL} = \gamma_S + \gamma_L - 2\sqrt{(\gamma_L^D \cdot \gamma_S^D) - 2\sqrt{(\gamma_L^P \cdot \gamma_S^P)}} \]

where \(\gamma_L^D, \gamma_S^D, \gamma_L^P\) and \(\gamma_S^P\) are the dispersive and polar components of the surface tensions of the liquid and solid, respectively.
The result equation of combining equation (3.1) and (3.5) is:

\[ \frac{\gamma_s (\cos \theta + 1)}{2 \sqrt{\gamma_p}} = \sqrt{\frac{\gamma_L}{\gamma_p}} \sqrt{\gamma_F} + \sqrt{\gamma_S}, \]

(3.6)

Because \( \gamma_s^d \) and \( \gamma_s^p \) are unknown, at least two liquids with known disperse and polar parts of the surface tension are required to determine the surface free energy of the solid wherein at least one of the liquids must have a polar part higher than 0. Normally, water, glycerol and formamide can be used as polar liquids and diiodomethane and \( \alpha \)-bromonaphthalene as dispersive. Table 3.12 shows the surface tension values for the three experimental liquids used.

**Table 3.12. Surface tension values for water, diiodomethane and ethylene glycol**

<table>
<thead>
<tr>
<th></th>
<th>( \gamma_L ) [mN/m]</th>
<th>( \gamma_F ) [mN/m]</th>
<th>( \gamma_S ) [mN/m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (H₂O)</td>
<td>22.1</td>
<td>50.7</td>
<td>72.8</td>
</tr>
<tr>
<td>Diiodomethane (CH₂I₂)</td>
<td>49.0</td>
<td>1.8</td>
<td>50.8</td>
</tr>
<tr>
<td>Ethylene glycol (C₆H₁₂O₂)</td>
<td>23.6</td>
<td>5.0</td>
<td>28.6</td>
</tr>
</tbody>
</table>

The surface free energy of the two modified and un-modified brush layer materials (hPS and PS(70\%)-PMMA) has been determined by the sessile drop method using the liquids described above. The values are depicted in Table 3.13. It can be observed that after oxygen plasma functionalization the substrate becomes more attractive to PMMA domains since the polar component of the free energy is larger. Moreover, for the strongest oxygen plasma conditions, it has not been possible to measure the value for the hPS brush probably because the film thickness was thinner (5.6 nm) than for PS(70\%)-PMMA (8.6 nm) and almost all brush was removed after the functionalization step.

On the other hand, the substrate was again characterized after the resist stripping with PGMEA in order to see if it induced some hydrophobicity to the surface. Nevertheless, the values of surface free energy in Table 3.14 show that there is almost no change on the surface after rinsing.

**Table 3.13. Surface free energy of modified and non-modified hPS and PS-r-PMMA brush layers.**

<table>
<thead>
<tr>
<th></th>
<th>( \gamma_L ) [mN/m]</th>
<th>( \gamma_F ) [mN/m]</th>
<th>( \gamma_S ) [mN/m]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>hPS</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non-modified</td>
<td>38.5±0.22</td>
<td>1.3±0.05</td>
<td>39.8±0.27</td>
</tr>
<tr>
<td>Modified (Conditions A)</td>
<td>31.3±0.14</td>
<td>20.4±0.12</td>
<td>51.7±0.26</td>
</tr>
<tr>
<td>Modified (Conditions B)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>PS-r-PMMA (70% PS)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non-modified</td>
<td>35.6±0.27</td>
<td>5.2±0.1</td>
<td>40.7±0.37</td>
</tr>
<tr>
<td>Modified (Conditions A)</td>
<td>34.5±0.27</td>
<td>14.6±0.14</td>
<td>49.1±0.41</td>
</tr>
<tr>
<td>Modified (Conditions B)</td>
<td>28.9±0.53</td>
<td>42.6±0.55</td>
<td>71.5±1.09</td>
</tr>
</tbody>
</table>
Table 3.14. Surface free energy of modified hPS and PS-r-PMMA brush layers after PGMEA rinsing

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$\gamma'_L$ [mN/m]</th>
<th>$\gamma'_T$ [mN/m]</th>
<th>$\gamma_L$ [mN/m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>hPS</td>
<td>Modified (Conditions A)</td>
<td>30.2±0.12</td>
<td>20.1±0.11</td>
</tr>
<tr>
<td></td>
<td>Modified (Conditions B)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PS-r-PMMA (70% PS)</td>
<td>Modified (Conditions A)</td>
<td>33.3±0.14</td>
<td>17.4±0.11</td>
</tr>
<tr>
<td></td>
<td>Modified (Conditions B)</td>
<td>28.8±0.07</td>
<td>40.6±0.15</td>
</tr>
</tbody>
</table>

The chemistry of the surface has been analyzed with X-Ray Photoelectron Spectroscopy (XPS) on both modified and un-modified surfaces to demonstrate the chemical affinity change on the polymer after the functionalization step. As shown in Figure 3.28,b, after oxygen plasma functionalization there is an increase in intensity towards higher binding energies in the ca. 286-291 eV region, which corresponds to contributions from different carbon-oxygen configurations, characteristic from the brush oxidation (blue, green and pink features corresponding to hydroxyl, carbonyl and carboxyl contributions, respectively).

![Figure 3.28. XPS spectra corresponding to C1s region of (a) hPS and (b) modified hPS using conditions A, by using a PHOIBOS150 analyser and monochromatic 1486.6 eV photons](image)

On the other hand, the surface has been also characterized by studying the BCP behavior on top of un-modified and modified brush layers. It is known that the neutral brush layer for lamellar PS-b-PMMA is PS$_{90\%}$-r-PMMA, denoting that it takes the fingerprint morphology on free-free-surfacesurface. Therefore, when using PS$_{90\%}$-r-PMMA the surface is affine to PS, and when it is modified, it changes its affinity to neutral or more PMMA affine due to the oxidation of the substrate.

To carry out the experiment, PS-b-PMMA 22 nm pitch BCP is spin-coated on the top of PS$_{90\%}$-r-PMMA brush from a 1.5% PGMEA solution and spin-coated at 1500 rpm. Then it is annealed at 230°C for 5 min. Figure 3.29 shows the BCP morphology on top of modified and non-modified PS$_{90\%}$-r-PMMA. From Figure 3.29.a it is observed that, as previously predicted by the surface free energy characterization, before the treatment the surface is slightly affine to PS and it changes its affinity to strongly attract PMMA when it is oxidized by the oxygen treatment (Figure 3.29.b and c). Despite having modified the affinity of the surface by chemically oxidizing it, in order to guide the BCP by using wide
guiding stripes, softer oxygen plasma conditions which creates a surface not strong but slight affine to PMMA are needed.

![Figure 3.29](image)

**Figure 3.29.** PS-\(b\)-PMMA (\(L_0 = 22\) nm) self-assembly on PS\(_{\text{hP}}\)-r-PMMA un-modified (a) and modified with *conditions A* and *B* (b and c, respectively)

### 3.4.2. Directed self-assembly by chemical epitaxy of PS-\(b\)-PMMA results

Nevertheless, the DSA process was anyway tested with “*conditions A*” depicted in Table 3.11 since these were the softest conditions available. As Figure 3.30 shows, the DSA process did not work because the resist is somehow modified during the functionalization process and conventional strippers are not efficient enough to remove the whole resist. Therefore, in the SEM images it is observed that BCP is blended with the rests of e-beam resist not allowing thus, the precise BCP DSA.

![Figure 3.30](image)

**Figure 3.30.** PS-\(b\)-PMMA (\(L_0 = 22\) nm) DSA on hPS chemical guiding patterns created when using oxygen plasma conditions *A*.

In order to demonstrate that the process is easily implementable at larger scales and that the problem is coming from the oxygen plasma equipment availability, the functionalization process has been performed at IMB-CNM in small samples from guiding patterns created at 300 mm. Thus, samples which had been previously patterned in a 300 mm e-beam tool have been functionalized at IMB-CNM by using the soft conditions depicted in Table 3.4.

The BCPs (38 nm, 28 nm and 22 nm pitch) and processing conditions have been the same as the ones used at CEA-Leti. Figure 3.31 shows the DSA results of the three BCPs aligned with CEA-Leti’s guiding patterns (\(L_a = 1.5L_0\) and \(L_0 = 0.5L_a\)). That proves, therefore, that
the process can be easily scaled to 300 nm almost without defects, although an accurate oxygen plasma condition has to be found. Moreover, as Figure 3.32 demonstrates, high density multiplication factors when using chemical epitaxy can be obtained (in all cases $L_e$ is constant to 1.5$L_0$, and $L_0$ is varied). The DSA results shown are for BCP length chains of 38 nm and 28 nm and density multiplication factors, up to 5$L_0$. As compared to the results obtained at IMB-CNMM for PS-b-PMMAs of 38 nm pitch, there have been obtained high density multiplication factors when using wide stripes. This is attributed to the different specifications of the brush layer used (hPS) which had a higher molecular weight, and a thus a thicker film.

**Figure 3.31.** PS-b-PMMAs DSA on chemical guiding patterns created at CEA-Leti and functionalized at IMB-CNMM (a) $L_0 = 38$ nm, (b) $L_0 = 28$ nm and (c) $L_0 = 22$ nm

**Figure 3.32.** PS-b-PMMAs DSA with density multiplication factors between 2 and 5$L_0$ for (a-d) 38 nm and (e-h) 28 nm pitch BCP
3.5. Development and implementation of chemical epitaxy by UV substrate functionalization

In this section, a novel approach of creating chemical guiding patterns by means of exposing the desired areas of the pattern to UV, is presented. It has been previously demonstrated that there is the need to tune the surface energies, to precisely control the orientation of the BCP morphology.\textsuperscript{35,36} When creating chemical guiding patterns, there is the need to chemically change the affinity of the guiding stripes. This can be performed by exposing the surface to a controlled oxygen plasma exposure\textsuperscript{33}, as demonstrated in the previous section, or by using two brush layer materials with different chemical affinities.\textsuperscript{18} However, this last approach presents the drawback of involving a large number of processing steps. On the other hand, when using oxygen plasma to functionalize the substrate, the process window is very tight.

Therefore, a new strategy to chemically modify the brush is presented. It consists on exposing the polymer surface to UV light, which undergoes to a photochemical reaction. It is known that UV photons interact with PS, leading to carbon-carbon scissions and generating C-O bonds (C-O, C=O, COOH...) at the polymer surface.\textsuperscript{37,38}

From surface characterization techniques, it has been demonstrated that the surface reactions which take place during the UV irradiation, result in a loss of aromacity, produced by the formation of radicals, PS cross-linking and oxidative degradation (Figure 3.33).\textsuperscript{39,40} Furthermore, it has been published that the level of oxidation during a UV exposure is less than during an oxygen plasma.\textsuperscript{35}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure33.png}
\caption{Photochemical reactions of PS due to UV exposure: (a) formation of radicals, (b) cross-linking and (c) oxidative degradation\textsuperscript{38}}
\end{figure}
Figure 1.2 shows XPS spectra of polystyrene, plasma-treated and UV-irradiated polystyrene from Zhang et al. work. It is observed that the main changes are due to the oxidation of the surface, more intense when the sample is exposed to oxygen plasma.

![Figure 3.34. XPS spectra of (a) polystyrene and (b) plasma-treated polystyrene and (c) UV-irradiated polystyrene, presented by Zhang et al.](image)

This means that, UV surface modification results in an easy a rapid approach to control the interfacial interactions providing a wider process window, as compared with conventional oxygen plasma treatments. Moreover, although the number of processing steps is higher than in the direct writing approaches because there is the need to use a resist, this method results very suitable to be implemented on a single track, thus making easier its industrial application.

3.5.1. Chemical surface characterization of UV exposed surfaces

3.5.1.1. UV exposure by using a lamp

In order to implement this approach to create chemical guiding patterns and align BCPs, the technique is first tried and characterized on free-surface. This work has been performed at CEA-Leti’s pilot line by using an UV lamp of the SOKUDO DUO lithography track. The overall process is depicted in Figure 3.35. The starting substrates are 300 mm silicon wafers (\{100\}, p-type), in which 30 nm SiARC and 95 nm SOC layers have been deposited.

Then, PS$_{700}$-$\tau$-PMMA and hPS brush layers have been used to perform the UV tests on 300 mm. Their specifications are depicted in Table 3.1. The brush layers have been spin-coated from a 2% PGMEA solution at 1500 rpm, and annealed at 230°C for 10 min. Consequently, in the same process step, the non-grafted brush is rinsed away with PGMEA, and the sample is exposed with a certain UV dose.

Finally, PS-$b$-PMMA of two molecular weights (depicted in Table 3.2), are deposited on top of the modified brush, and annealed in the same track at 230°C for 5 min.
Figure 3.35. Schematic of the PS-b-PMMA self-assembly process on UV modified brush polymers.

Figure 3.36 and Figure 3.37 show SEM images of PS-b-PMMA self-assembly, on top of different UV exposed hPS and PS-\(\sigma\)-PMMA surfaces, respectively. When hPS brush is used (Figure 3.36), it can be observed that the surface without UV exposure is, as expected, PS affine. Nevertheless, the surface becomes neutral when it is briefly exposed to UV dose, as fingerprint morphology SEM images reveal (from 10 to 80 mJ/cm\(^2\) dose of process window). At doses higher than 80 mJ/cm\(^2\), the brush is overexposed and it becomes more PMMA affine. It can be also drawn, that when higher molecular weight BCPs are used, the process window becomes narrower (at doses higher than 20 mJ/cm\(^2\), the surface starts being PMMA affine).

On the other hand, these results have been compared with PS\(70\%\)-r-PMMA brush. Figure 3.37 shows the self-assembly results when using PS\(70\%\)-r-PMMA. As the brush is PS affine, when there is no exposure, the surface is more attractive to PS. Nevertheless, when it is briefly UV exposed it becomes rapidly PMMA attractive, without going through a neutral affine state. Since UV tends to react with PS inducing its cross-linking and oxidation, making it little by little more PMMA affine, the process window when using PS\(70\%\)-r-PMMA, is narrower due to its lower PS content.

Figure 3.36. PS-b-PMMA self-assembly as a function of UV dose on hPS brush.
3. Directed self-assembly of PS-b-PMMA block copolymers by chemical epitaxy

![Figure 3.37](image)

**Figure 3.37.** PS-b-PMMA self-assembly as a function of UV dose on PS-r-PMMA brush

### 3.5.1.2 UV exposure by using a laser

In order to test the impact of the UV exposure on the surface interactions, another UV source has been used. The experiments have been performed in a DUV tool, Nikon 5307E, which operates at a wavelength of 193 nm.

Both, the starting substrates and processing conditions have been the same as the ones described in the last experiments. Figure 3.38 and Figure 3.39 show the results of PS-b-PMMA of 22 nm and 38 nm, respectively. As observed for both BCPs, the process window is wider than when using the UV lamp. On the other hand, the exposure doses are a little bit higher due to the difference on the light wavelength.

![Figure 3.38](image)

**Figure 3.38.** PS-b-PMMA ($L_0 = 22$ nm) self-assembly as a function of UV dose ($\lambda = 193$ nm) on hPS brush (Scale bar corresponds to 500 nm)
Figure 3.39. PS-b-PMMA self-assembly ($L_0 = 38$ nm) as a function of UV dose ($\lambda = 193$ nm) on hPS brush (Scale bar corresponds to 500 nm)

Furthermore, as the process window becomes wider when varying the light wavelength, the experiments have been also tried when using PS-$r$-PMMA brush. Figure 3.40 shows the PS-$b$-PMMA self-assembly when modifying PS$_{2000}$-$r$-PMMA brush with a UV light source of ($\lambda = 193$ nm).

As observed in the images, and in agreement with the results for hPS brush, the process window in which the surface is neutral, is wider than when modifying the surface with the UV lamp. Moreover, as also already observed in the last experiments, when comparing both BCPs, the process window is wider when using the lowest molecular weight material.

Figure 3.40. PS-b-PMMA self-assembly as a function of UV dose ($\lambda = 193$ nm) on PS-$r$-PMMA brush

On the other hand, in order to study the effect of the antireflective layer on the PS modification, there has been performed a test on a silicon substrate. This test has been done with PS-$b$-PMMA of 22 nm and 38 nm on hPS brush surfaces. The obtained results are shown in Figure 3.41, for 38 nm BCP pitch.

It is interesting to observe from the results, that the process window has been considerably reduced, and shifted to lower doses. This effect is explained due to the absence of the antireflective layer. It is known that a high reflective substrate like silicon, can cause light from the exposure to bounce back into the brush. This effect is however, mitigated when using an antireflective coating, since it absorbs part of the UV light. Therefore, during the UV exposure, the energy is partially absorbed by the ARC, and then the effect on the
brush layer is reduced. Table 3.15 summarizes the process window in terms of UV dose, for each BCP as a function of the UV source, brush layer and substrate.

![Figure 3.41. PS-b-PMMA self-assembly (L0 = 38 nm) as a function of UV dose (λ = 193 nm) on hPS brush when using a silicon substrate (Scale bar corresponds to 500 nm)](image)

<table>
<thead>
<tr>
<th>UV Lamp (SiARC/SOC)</th>
<th>UV Laser (SiARC/SOC)</th>
<th>UV Laser (Si)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hPS PS&lt;sub&gt;80/20&lt;/sub&gt;-r-PMMA</td>
<td>10 - 80 mJ/cm&lt;sup&gt;2&lt;/sup&gt;</td>
<td>200 - 320 mJ/cm&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>22 nm</td>
<td>-</td>
<td>40 - 120 mJ/cm&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>38 nm</td>
<td>-</td>
<td>100 - 220 mJ/cm&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

3.5.2. Surface free energy characterization

In order to further characterize the surface exposed to UV light and have a more quantitative result, the surface free energy has been analyzed. The surface characterization has been performed by using the sessile drop method, described previously in section 3.4.1.4. The UV exposure method to carry out the characterization has been performed with the lamp due to the easiest accessibility to the tool.

The analysis of the UV exposure has been performed on different treated hPS and PS<sub>80/20</sub>-r-PMMA samples. Figure 3.42 represents the total surface free energy, \( \gamma \), as a function of the UV dose for both brush materials. As observed, for both materials, the increase of surface free energy with the UV exposure dose is exponential, but much more slower for hPS. This allows determining a process window for hPS (dashed line), whereas it is not possible for PS<sub>80/20</sub>-r-PMMA. In Figure 3.43, there is a further characterization of the hPS brush layer, representing the two components (polar and dispersive) of the surface free energy. As clearly observed from the graph, the major change on the surface free energy is due to the polar component, owing to the oxidation reaction taking place at the surface.

On the other hand, the surface free energy value in which the surface is neutral to both homopolymers, has been considered to be the corresponding for the lamellae neutral brush
layer, PS$_{60 \%}$-$r$-PMMA, which corresponds to a polar surface free energy, $\gamma_P$, of 5.2 mN/m. The horizontal dashed line on the graph represents the value of the polar surface free energy of PS$_{60 \%}$-$r$-PMMA. As observed it fits inside the process window in which the hPS presents a neutral behavior.

**Figure 3.42.** Surface free energy - UV dose curve plot performed on hPS and PS$_{60 \%}$-$r$-PMMA samples exposed to UV lamp (dashed line represents the process window for hPS brush)

In addition, the surface has been also characterized by XPS. There have been studied three UV-exposed samples, and the chemical changes have been compared with bare PS. As shown in Figure 3.44, after the UV functionalization, there is an increase in intensity
towards higher binding energies, which corresponds to the contributions of carbon-oxygen bonding. Nevertheless, the oxidation level present on the surface is much more lower than the one observed when the sample was oxidized by oxygen plasma (Figure 3.28.b). This is in agreement with the statement, that UV modification allows getting a wider processing window than the one provided by other functionalization methods.

**Figure 3.44.** XPS spectra corresponding to C1s region of different UV exposed hPS surfaces, using a PHOIBLOS150 analyser and monochromatic 1486.6 eV photons

### 3.5.3. Directed self-assembly of chemical epitaxy by UV surface functionalization

#### 3.5.3.1. Description of the chemical epitaxy process

In order to find the final DSA application with this novel approach, the surface and the BCP self-assembly behavior, have had first to be characterized. The overall implemented DSA chemical epitaxy process is the one depicted in Figure 3.45. It consists of 6 steps: (i) brush spin-coating, (ii) DUV lithography on negative tone resist (NTR), (iii) resist development, (iv) UV exposure, (v) resist stripping and (vi) BCP spin-coating.

**Figure 3.45.** Schematic of the chemical epitaxy process based on DUV and UV functionalization implemented at Leti’s pilot line
3.5.3.2. *Substrate preparation and creation of the chemical guiding patterns*

The DSA process has been performed with the same substrates and materials, as the ones used for the surface characterization. First, in order to optimize the lithography step, a Focus/Energy matrix (FEM) is performed.

Then, the substrate is prepared, and an hPS brush layer is deposited on the top of the surface in order to define the chemical guiding patterns on it. The 193d lithography is performed by using a NTR, *JSR AIM8630JN*, which is pre-baked at 85°C for 1 min. Consequently, the 193d lithography is performed in a *Nikon 5307E* tool, with a dose of 51 mJ/cm². Subsequently, the resist is post-baked at 85°C for one further minute, and developed with butyl acetate.

Once the lithography is performed, the substrate is chemically modified by exposing the sample to the UV lamp at 20 mJ/cm², since it is the value in which the surface presented a neutral surface. Finally, the resist is stripped with IPA, and PS-β-PMMA of 22 nm pitch is deposited and annealed.

Nevertheless, when the wafer was inspected, there was no evidence of chemical pattern and the entire surface seemed to be PS affine. Therefore, the effect of the resist stripping on the UV modified surface was inspected by characterizing its surface free energy. Table 3.16, shows the values of the surface free energy of different treated hPS surfaces. As commented previously, the surface free energy increases after UV exposure, but it turns back to the reference value after dipping the sample in BA or IPA. This is attributed mainly to a change on the polar component of the surface free energy which decreases considerably. This is explained because the solvents used to strip the resist, affect the chemical changes performed on the surface by stripping the polar groups created on the brush layer. Looking at the surface free-energy values, it is clarified therefore, the fact that there is no chemical contrast on the guiding patterns when using 20 mJ/cm².

**Table 3.16. Surface free energies of different hPS treated surfaces**

<table>
<thead>
<tr>
<th></th>
<th>hPS</th>
<th>hPS + UV</th>
<th>hPS + UV + BA</th>
<th>hPS + UV + IPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ</td>
<td>39.8 mN/m</td>
<td>48.5 mN/m</td>
<td>38.8 mN/m</td>
<td>38.8 mN/m</td>
</tr>
<tr>
<td>ηθ</td>
<td>38.5 mN/m</td>
<td>33.3 mN/m</td>
<td>37.9 mN/m</td>
<td>37.9 mN/m</td>
</tr>
<tr>
<td>ηηη</td>
<td>1.3 mN/m</td>
<td>9.2 mN/m</td>
<td>0.9 mN/m</td>
<td>0.8 mN/m</td>
</tr>
</tbody>
</table>

The solvent effect on different UV doses, has been widely studied by characterizing the surface free energy, in order to force the contrast on the chemical guiding patterns. The optimal value found, which is within the hPS process window and which does not damage the brush layer (the brush thickness remains the same) has been to 50 mJ/cm². When using this dose, the surface free energy after stripping the resist with IPA is 43.8 mN/m, which is within the hPS process window (see Figure 3.42). The DSA results are shown in Figure
3. Directed self-assembly of PS-b-PMMA block copolymers by chemical epitaxy

3.46, where the darker areas are the ones covered by the NTR (non-modified and PS-affine).

![Figure 3.46](image)

**Figure 3.46.** Schematic of the chemical epitaxy process based on DUV and UV functionalization implemented at Leti’s pilot line

In summary, it has been demonstrated a viable process to create chemical guiding patterns, which allows using a wider process window. This method allows controlling with precise accuracy the interactions between the guiding pattern and the BCP blocks by properly tuning the UV exposure dose. Therefore, it permits avoiding non-desired morphologies as may appear with the oxygen modification approach. However, as it has been demonstrated by the surface free energy characterization, the effect of the solvents during the processing has to be taken into account.

3.6. Chemical epitaxy based resistless direct writing methods

3.6.1. Introduction

Direct writing methods involve the preparation of the desired patterns avoiding any issues related with resists. In these methods, the radiation that is used to expose the surface is not transmitted through a resist but directly to the substrate. Direct writing techniques can achieve resolutions below 6 nm, high precision for pattern placement and a reduction in the number of process steps because the use of a resist is not needed.

Two novel methodologies based on direct writing lithography have been developed and optimized. The guiding patterns are directly created on the top of the brush layer inducing its chemical modification by means of EBL and AFM.

3.6.2. E-beam lithography direct writing

EBL is normally used in surfaces covered with electron-sensitive films, since the electron beam changes the chemistry of the resist, enabling the selective removal of the exposed or non-exposed regions. Despite being a limiting technique for high-volume production due to its low throughput, the major advantage of EBL is that patterns below 10 nm resolution
can be exposed. Therefore, this makes it a very suitable technique for research and development.

3.6.2.1. Materials and methods

Description of the chemical epitaxy process

In a conventional EBL, the step sequence of depositing, developing and removing the resist makes the process larger and may induce some chemical changes on the substrate and its functionalization. In direct e-beam writing, the creation of the guiding patterns is performed by directly exposing the polymer brush layer to electrons in order to induce its chemical modification, without the use of a resist. Indeed, by accurately tuning the e-beam parameters, highly precise and resolution patterns can be created, which is one of the critical factors in the microelectronics industry. Besides this, the developed process of e-beam direct exposure becomes simpler since the sequence of resist deposition, exposure, development, substrate functionalization and resist strip is substituted by a single step.

Figure 3.47 shows the overall fabrication process for PS-b-PMMA DSA using guiding patterns created by direct e-beam exposure on top of the brush layers made of PS-OH. It consists of a three-step process: (i) PS-OH brush grafting on top of silicon substrate, (ii) creation of guiding patterns by e-beam exposure and (iii) BCP self-assembly.

1. Silicon substrate  
2. Brush spin-coating  
3. E-beam direct writing  
4. BCP spin-coating

![Figure 3.47. Overall fabrication process for DSA by e-beam direct writing](image)

Brush and block copolymer materials

The starting substrates are 0.9 x 0.9 cm chips bearing a native silicon oxide layer (p-type silicon wafers of 4-40 $\Omega \cdot \text{cm}$ resistivity). The brush layer used is PS-OH with a $M_n = 4.5$ kg·mol$^{-1}$ and PDI = 1.09, purchased from Polymer Source, Inc and the BCP material is PS-b-PMMA of 28 nm pitch. The specifications of both the brush and the BCP are depicted in Table 3.17.

<table>
<thead>
<tr>
<th></th>
<th>Molecular weight</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-OH</td>
<td>4.5 kg/mol</td>
<td>1.34</td>
</tr>
<tr>
<td>Lamellar PS-b-PMMA</td>
<td>45 kg/mol</td>
<td>1.12</td>
</tr>
</tbody>
</table>
Substrate preparation and creation of chemical guiding patterns

In a first step, a 40 nm thick PS-OH layer from a 1.5% toluene solution is spin-coated at 5000 rpm for 1 min on the top of a silicon substrate which has been previously activated by using oxygen plasma at 500W for 10 min in order to enable the reaction between the hydroxyl PS-OH groups and the native oxide of the surface. In order to accelerate the reaction, an annealing step at 260°C for 5 min in a continuous N₂ gas flow. It is important to avoid oxygen during the annealing step, since it could react with the brush layer producing its oxidation and thus, inducing a chemical modification that could affect after to the DSA process.

After, the non-reacted PS-OH brush is rinsed away with toluene by ultrasounds bath at 40°C for 5 min, leaving a grafted 4.7 nm PS-OH film. Then, the chemical guiding patterns are created on the grafted PS-OH by direct e-beam exposure in a RAITH150Two tool without using any kind of resists. The e-beam process is performed by exposing the desired patterns at 20 kV and 330 pA of beam current with a nominal beam diameter of 2 nm. On the other hand, a wide range of e-beam factors, between 4 mC/cm² and 4 C/cm², has been studied in order to find the optimal width of the guiding stripes that guide the assembly of the BCP. This means that the line writing speed is varied between 0.825 and 0.0001 mm/s by using a line step of 10 nm. The exposure is defined as a set of single line exposures. The pattern pitch employed is 4L₀ (where L₀ is the BCP pitch), and the widths of the guiding and background stripes are determined by the dose factor applied in each case. Figure 3.48 shows the chemical guiding patterns specifications for a 4L₀ pattern pitch, in which Lₑ and L₀ represent the guiding and background stripe widths, respectively. In all the tests, the pattern pitch has been set at 4L₀, and the guiding stripe width is defined by the dose factor.

![Figure 3.48](image)

Figure 3.48. Chemical guiding patterns specifications created by direct e-beam writing. Schemes represent (a) wide and (b) narrow guiding stripes exposed. The guiding stripes are colored in magenta and the pristine PS-OH surface in brown. L₀ refers to the pitch of the BCP and Lₑ to the separation between guiding stripes.

In order to see how the guiding patterns look like after e-beam exposure, an array of 112 nm pitch lines (4L₀) with a line width of 42 nm (1.5L₀) which corresponds to an e-beam dose of 184,000 μC/cm², has been characterized by AFM, as it is shown in Figure 3.49. It is important to highlight that the contrast in the phase image (Figure 3.49.c) is larger than in the topographic image (Figure 3.49.a), indicating that the guiding pattern creation mainly involves a brush chemical change. On the other hand, the observed topographic
change may be an artifact due to the effect of the chemical change on the interaction forces between the tip and surface that determine how the amplitude of the tip oscillation is reduced.

**Figure 3.49.** AFM images and profiles of guiding patterns created by e-beam direct exposure (20 kV, 30 μm, 184,000 μC/cm²) (a) Topographic AFM image of an array of 112 nm pitch (Δz = 2 nm) and (b) extracted average profile (c) Phase AFM image acquired simultaneously to image (a) (ΔΦ = 4 Deg) and (d) extracted average profile

In order to characterize the chemical affinity between the different areas of the guiding pattern and each domain of the BCP, the contact angle between homopolymers, polystyrene (PS) and poly(methyl methacrylate) (PMMA), with the brush has been experimentally determined.

Figure 3.50 shows the procedure to determine the chemical interaction characterization between different species and it consists of depositing a thin homopolymer layer on top of both unmodified and modified brush. The samples are annealed at 190°C for 24h in a vacuum environment in order to accelerate the dewetting of the polymer. Droplets of the homopolymer are formed on top of brush layer, and then the contact angle of these droplets is determined by AFM as depicted in Figure 3.50. As it is revealed in the figure, e-beam exposed areas present larger affinity to PS domains. This is explained by the cross-linking of PS due to e-beam exposure, as reported in the literature. PS is found to be resistant to electron beams, but beyond a certain e-beam dose, it undergoes cross-linking with the possible scission of the phenyl groups.

1. E-beam DW based guiding patterns
2. Homopolymer spin-coating
3. Homopolymer dewetting

**Figure 3.50.** Overall fabrication process to determine the contact angle between homopolymers and brush
3. Directed self-assembly of PS-b-PMMA block copolymers by chemical epitaxy

![Figure 3.51](image1.png)

**Figure 3.51.** Procedure to determine the contact angle between homopolymers and the brush layer (e-beam modified and un-modified) (a) Topographic AFM image of PS droplets on top of patterned and unpatterned areas (b) Profile of a PS droplet on PS-OH

**PS-b-PMMA spin-coating**

After e-beam parameters were optimized to achieve the precise guiding pattern dimensions ($L_a = 1.5L_0$ and $L_b = 2.5L_0$), a lamellar PS-b-PMMA BCP of 28 nm pitch from a 1.15% toluene solution is spin-coated at 2750 rpm for 1 min. Afterwards, in order to promote the self-assembly, the sample is annealed at 200°C for 20 min in hot-plate.

3.6.2.2. Directed self-assembly by chemical epitaxy of PS-b-PMMA results

Figure 3.52 shows the DSA results for a 28 nm BCP when different e-beam doses were applied to create the chemical guiding patterns. It can be seen that the best alignment of the BCP is achieved when a dose factor of 184,000 μm/cm² is used (Figure 3.52c), which corresponds to a guiding stripe width of 1.5L₀ and a density multiplication factor of 4L₀.

![Figure 3.52](image2.png)

**Figure 3.52.** DSA of PS-b-PMMA of 28 nm pitch for different e-beam doses. (a) dose = 256,000 μC/cm²; (b) dose = 196,000 μC/cm²; (c) dose = 184,000 μC/cm²; (d) dose = 40,000 μC/cm²

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As discussed previously, in accordance with contact angle results it can be better observed in the zoomed image (Figure 3.53) that on the top of exposed areas (red stripes) there are two PS domains and one PMMA domain in the middle, indicating that the e-beam modified surface has become slightly more affine to PS. This behavior is better described in the scheme where one block of PMMA (red colored) is at the center of the guiding stripe, while two PS domains (blue colored) also stand on the top of the guiding stripe, thus demonstrating the slightly affinity of the guiding stripes to PS. In chapter 6 the chemical interactions taking place between the domains and the chemical guiding pattern are discussed in more detailed from HAXPES experiments characterization.

![Figure 3.53](image)

**Figure 3.53.** Zoom SEM image of PS-β-PMMA DSA ($L_0 = 28$ nm) for an e-beam dose of 184,000 μC/cm². Guiding stripes are colored in red (1.5$L_0$) and the pristine PS-OH surface in blue (2.5 $L_0$)

### 3.6.3. Local Anodic Oxidation based AFM nanolithography

Aside from e-beam lithography, AFM-based local anodic oxidation (LAO) can be used as a direct lithography approach. In contrast with e-beam direct writing, in which the high e-beam doses employed prevent from high resolution guiding patterns and involve large e-beam writing times, the unique capabilities of AFM, in terms of resolution and position accuracy, makes it very suitable for the investigation of the guiding behavior of novel polymer materials, in view of obtaining a half-pitch resolution around 10 nm or below.

Few efforts of creating guiding patterns by means of AFM lithography for DSA applications have been previously reported. In these works, a self-assembled layer of octadecyltrichlorosilane (OTS) was chemically modified by contact-mode AFM while applying a voltage and then cylindrical BCP were directly self-assembled on top of it.

LAO is a modality of AFM lithography in which a voltage is applied between the tip and the surface that leads to an electrochemical reaction. As depicted in Figure 3.54, for a silicon substrate and under certain environment conditions, between the tip and the surface there is always a water absorption layer which covers both the tip and the substrate. When the tip is approached some nanometers to the surface a water meniscus is formed, and then by applying a voltage an electrochemical cell, in which the tip acts as a cathode and the water as the electrolyte, is generated.
The chemical reactions that take place in the cell are water hydrolysis and the subsequent oxidation of the silicon. The overall reaction is depicted in (3.7).

\[
\text{Si} + 2\text{OH} \rightarrow \text{SiO}_2 + 2\text{H}^+ + 4e^- \tag{3.7}
\]

LAO is performed by operating AFM in noncontact mode, increasing thus the tip throughput and lifetime.\(^{48}\)

![Figure 3.54. Local anodic oxidation steps in noncontact mode](image)

The application of LAO AFM method can be used as a technique to create chemical guiding patterns on top of a brush layer by increasing the tip throughput and lifetime.\(^{48,49}\) Furthermore, patterns with density multiplication factors up to 7 can be created in a very efficient, precise and routinely way by using commercial equipment. On the other hand, because of the achievable resolution of oxidation scanning probe lithography, this approach has great potential to become very useful to study next generation DSA of BCP.

### 3.6.3.1 Materials and methods

**Description of the chemical epitaxy process**

Figure 3.55 shows the overall process for the fabrication of chemical guiding patterns on top of PS-OH brush layers by LAO. It consists in a three-step process: (i) PS-OH brush grafting on top of silicon substrate, (ii) creation of guiding patterns by AFM-based LAO and (iii) BCP self-assembly.

As in the case of e-beam direct writing, the whole process contains fewer single processes than the normal methods used to create guiding patterns, since the sequence of resist, exposure, development and resist removal is discarded/eliminated by the single process of o-SPL patterning.

![Figure 3.55. Overall fabrication process for DSA by o-SPL](image)
Brush and block copolymer materials

To directly compare both direct writing techniques, the same materials (brush and BCP) and processing conditions are used in the fabrication process.

When using the LAO-AFM based approach, the chemical guiding patterns are created directly on top of PS-OH after being removed the non-reacted brush with toluene.

Substrate preparation and creation of the chemical guiding patterns

The AFM instrument (Dimension Icon, Bruker) is operated under noncontact mode using standard tapping cantilevers (OTESPA with nominal tip radius of 7 nm), with a close loop control of x, y and z displacement which avoids piezo-induced dimensional distortions. A homemade humidity control system is used in order to control the humidity during the oxidation process. As depicted in Figure 3.56, it maintains the humidity constant in the range of 20-60% by introducing inside the chamber a constant N₂ flow.

![Humidity control system](image)

**Figure 3.56.** Humidity control system installed next to the AFM chamber

In order to create the chemical guiding patterns the AFM is operated in soft-tapping mode, at an oscillation amplitude around 15 nm and then moved to the desired position to start the creation of a line. After, the feedback loop is disconnected and a positive voltage is applied to the sample through the AFM chuck. When the voltage pulse is applied, the electric field induces the formation of a liquid meniscus between the sample and the tip in which a redox reaction takes place.

During the oxidation process, the tip is moved along the line at a selected speed, and when it reaches the end of the line the bias voltage is switched to zero and the feedback loop is connected (the feedback is off during writing). When the voltage is off, the liquid meniscus is broken and the tip recovers its original amplitude and it is moved to the new position to fabricate a new line.
It is important to highlight that in order to maintain constant the separation between the tip and the surface, the lines are fabricated following the direction where the lateral movement of the tip is parallel to the surface.

Figure 3.57 shows a scheme in which the local oxidation process is used when a polymer brush layer is grafted on top of a silicon substrate. Under the application of a voltage to the sample with respect to the tip, the water molecules are ionized (2H$_2$O $\rightarrow$ 2 OH$^-$ + 2H$^+$) and the OH$^-$ ions are accelerated through the surface where the electrochemical reaction takes place oxidizing the underneath silicon.

![Figure 3.57. Local anodic oxidation process on polymer brush layer](image)

Figure 3.58 shows an example of a large 15 x 15 μm$^2$ guiding pattern made up of an array of lines of 400 nm pitch. The magnified image reveals that the pattern consists of 15 nm width lines and roughly 1 nm height. The fact that the modified areas appear raised from the background indicates that the underneath silicon has been oxidized.

![Figure 3.58. AFM images and profile of high resolution guiding patterns created by o-SPL (a) Array of lines covering an area of 15 x 15 μm$^2$](image)

The resolution of the guiding patterns is determined by the AFM radius, the water meniscus size and the relative velocity of the tip with respect to the surface. By keeping constant the humidity, the tip-speed and the gap between the tip and the surface, it can be observed in Figure 3.59 that the higher the bias voltage applied, the wider the oxidized lines are. Therefore, the bias voltage has to be precise in order to control the accurate and desired line width. On the other hand, the line width can be also tuned by varying the humidity and keeping constant all other parameters, as it is seen in Figure 3.60, where the relative humidity used is 20% and 40%, respectively.
3. Directed self-assembly of PS-b-PMMA block copolymers by chemical epitaxy

Figure 3.59. AFM images of guiding patterns created by α-SPL at bias voltages of (a) 39.6 V, (b) 43.2 V, (c) 46.8 V and (d) 50.4 V, by keeping a constant humidity of 17%, a tip-speed of 2 μm/s and a tip-surface distance of 6 nm.

Figure 3.60. AFM images of guiding patterns created by α-SPL at (a) 40% and (b) 20% humidity, by keeping a constant bias voltage of 32.4 V, a tip-speed of 5 μm/s and a tip-surface distance of 8 nm. Red and black profiles in (c) correspond to low and high humidity, respectively, in order to highlight the effect of relative humidity on the guiding pattern creation.

High resolution guiding patterns are achieved when high tip velocity and low humidity are used. Figure 3.61 shows an example of high resolution guiding patterns consisting of an array of lines of 20 nm pitch with a line width resolution below 10 nm. It is remarkable that the contrast in the phase image is larger than in the topographic image, showing that the patterning involves changes in the surface chemical properties. The origin of compositional contrast in phase imaging AFM is related to changes in energy dissipation, meaning that in the oxidized regions of the pattern the tip dissipates more energy. This is also indicative of differences in the chemical and/or physical properties between the oxidized and non-oxidized regions. A closer inspection of the patterns reveals that its roughness is basically due by the surface roughness of the brush layer, which is the limiting factor for the present pattern resolution.
3. Directed self-assembly of PS-b-PMMA block copolymers by chemical epitaxy

![Image](image.png)

**Figure 3.61.** Topographic and phase AFM images of an array of lines of 20 nm pitch ($\Delta z = 4$ nm) and the respective profiles.

The guiding patterns created by o-SPL on the brush layer can be of diverse chemical/physical nature depending on the oxidation conditions used: (i) chemical surface modification of the top brush polymer chemical groups (similar to what it has been reported on tip-induced electro-oxidation for constructive nanolithography\(^{51}\)), (ii) chemical modification of the brush and oxidation of the underlying silicon and (iii) oxidation of the underlying silicon together with the brush polymer degradation.

When the first situation occurs, there is only a slight change not in topography but in phase AFM images, which means that there is no underneath oxide grown. In order to prove that there is only a chemical change on the surface, an additional experiment has been performed. Specifically, square type guiding patterns are formed at low oxidation conditions on top of PS-OH brush layers and then they are characterized using the peak-force tapping mode of the AFM. Figure 3.62 shows AFM topography (a) and adhesion (b) images with two squares patterns oxidized at 8V and 5V, respectively, by keeping constant all other parameters. Whilst enough contrast for the square oxidized at highest voltage is observed in both topography and adhesion images, the bottom AFM topography image (Figure 3.62a) reveals that there is not enough contrast for the square oxidized at the lowest voltage. On the other hand, the bottom AFM adhesion image (Figure 3.62b) shows a slightly contrast, indicating the presence of a chemically modified surface. Friction AFM images were not used since it has been observed that scanning in contact mode induces some chemical and topographical changes on the brush layer.
In order to prove when the second and third situations take place, the PS-OH stability to hydrofluoric acid (HF) has been tested. It is known that at 5% concentration and at 20°C, PS-OH is not altered under HF attack\textsuperscript{22}, thus it protects the silicon oxide grown by o-SPL to be etched. However, when the PS-OH becomes degraded because of the effect of applying high voltages, it loses its resistivity to HF and the underlying oxide reacts to HF.

To test the PS-OH resistance to HF, o-SPL has been performed on a PS-OH sample by using different bias voltages. Figure 3.63a and b show the topographic and friction AFM images before HF dipping for 10 seconds, and it can be observed that for medium voltages, the patterns show a good chemical contrast. However, in Figure 3.63b it is observed that for bias voltages higher than 34 V, the chemical contrast is large but the pattern does not sustain the HF etching. In that case, the patterns appear to be as a depressed area after HF etching, and the depth of the depression is consistent with the thickness of the brush layer (4.7 nm) and the native silicon oxide (1-2 nm). In consequence, it can be concluded that the use of high voltages damages the polymer layer inducing its degradation.

Figure 3.62. Peak-Force tapping AFM images corresponding to squared patterns created by o-SPL at bias voltages of 8 V (top square) and 5 V (bottom square)

Figure 3.63. AFM images of chemical patterns performed on a PS-OH by o-SPL at different bias voltages. Images (a) and (b) show the topography and phase images of the sample before HF etching, and (c) shows the topography image after immersing the sample in an HF solution for 10 seconds
PS-b-PMMA self-assembly

After optimizing the AFM lithography to achieve the precise guiding pattern specifications, a lamellar PS-b-PMMA BCP of 28 nm pitch from a 1.15% toluene solution is spin-coated at 2750 rpm for 1 min.

Afterwards, in order to promote the self-assembly, the sample is annealed at 200°C for 20 min in hot-plate.

3.6.3.2. Directed self-assembly by chemical epitaxy of PS-b-PMMA results

Figure 3.64 shows the results of PS-b-PMMA (L₀ = 28 nm) DSA when using o-SPL for the fabrication of guiding patterns. Figure 3.64.a shows a comparison between the guiding pattern (top, AFM topography image) and the BCP DSA (bottom, SEM image) for different multiplication factors.

The guiding pattern consists of an array of lines with variable pitch in order to demonstrate the different multiplication factors achievable for this BCP. The line width has been set to 14 nm which is the halfpitch of the BCP used, and density multiplication factors between 3L₀ and 5L₀ have been tested. On the other hand, Figure 3.64.b demonstrates the effectiveness of the o-SPL for BCP DSA, in which the boundary between the fingerprint and the aligned area is perfectly differentiated.

![Figure 3.64](image)

**Figure 3.64.** Different density multiplication factors for PS-b-PMMA BCP (L₀ = 28 nm) with chemical guiding patterns created by o-SPL (V = 36 V, tip-speed = 3 μm/s and RH = 23%) (a) Comparison between the guiding pattern (top, AFM topography image) and the aligned BCP (bottom, SEM image) SEM images have been taken after removing PMMA domains by oxygen plasma etching (b) SEM image showing the aligned BCP on top of the guiding pattern and the non-aligned BCP on top of unpatterned area.

In order to obtain higher density multiplication factors, the oxidation strength has to be increased since the conditions used to align the BCP in Figure 3.64 do not have the oxidation strength needed to enforce the BCP DSA with a density multiplication factor of
7L₀. However, when the oxidation strength is increased (by increasing the humidity or the bias voltage), the line width becomes wider and larger than the half BCP pitch, and thus 1.5L₀ lines width have to be created in order to not promote the alignment of only one BCP stripe, but three. Figure 3.65.a shows an example of a chemical guiding pattern created to achieve a 7L₀ density multiplication factor for PS-b-PMMA of 28 nm pitch. The pattern consists of an array of 196 nm pitch lines. As it can be better observed in the zoomed image (Figure 3.65.c), the oxidized lines appear wider than in previous showed DSA results in order to promote the alignment with high density multiplication factor.

On the other hand, the experiments point out that the simple chemical modification of the brush layer (oxidation conditions (j)) is not enough to induce the BCP alignment, while patterns showing at least 0.5 nm of topographic height contrast, efficiently allows its alignment. The influence of topography-induced alignment on chemical patterns has been previously reported⁵³.

A closer inspection of the aligned patterns discloses that there are three aligned stripes on the top of the oxidized line (one PMMA stripe surrounded by two PS stripes) indicating that the oxidized lines become not strongly but slightly affine to PS domains. This behavior is better depicted in the scheme of Figure 3.65.d and later on, explained and demonstrated by surface characterization techniques. This situation is different from the one reported in other works of BCP DSA by using AFM lithography⁵⁴,⁵⁵, where the oxidized areas become more PMMA affine. In these works, an octadecyldichlorosilane (OTS) self-assembled monolayer is used, instead of PS-OH, and the methyl layer is transformed to a carboxylic terminated layer, which is more affine to PMMA.

![Figure 3.65](image.png)

**Figure 3.65.** (a) AFM image of chemical guiding pattern created by o-SPL (V = 34.2 V, tip-speed = 2 μm/s and RH = 38%). (b) SEM image of PS-b-PMMA DSA with 7L₀ density multiplication factor. (c) Comparison between the guiding pattern (top, AFM topography image) and the aligned BCP (bottom, SEM image). (d) Scheme of the DSA process by o-SPL for high density multiplication factors. SEM images have been taken after removing PMMA domains by oxygen plasma etching.
3.6.4. Summary and comparison

In summary, two methods based on the creation of a chemical guiding pattern directly on the brush layer without using a resist have been presented. Both methods have the advantage of simplifying the processing sequence by reducing the number of single processing steps.

On the one hand, by e-beam direct writing it has been demonstrated that the dimensions of the guiding patterns can be controlled with accuracy by varying the e-beam dose and with a much more simpler processing than other methods reported in the literature. However, the major drawback is the low throughput coming from the high e-beam doses employed to chemically modify and cross-link the structure of PS.

On the other hand, DSA by AFM-based nanolithography process relies on the unique resolution performance of AFM, although it has low throughput arising from the limited scan size and speed, which at present, limits its industrial application. However, diverse actions are taken in order to improve it, such as parallelization of AFM lithography by the use of multiple probes\textsuperscript{56} or the use of local oxidation of high-resolution stamps.\textsuperscript{57,58} Moreover, it is a very promising technique to study the behavior of high-$\chi$ BCP which have half-pitches below 10 nm, since line widths of 7 nm can be obtained under controlled environmental and processing conditions.

In any case, the creation of guiding patterns either by o-SPL or direct writing EBL are a rather simple and affordable methods to study the alignment behavior of BCPs.
3.7. Summary and conclusions

Three different approaches based on chemical epitaxy processes have been designed and implemented at IMB-CNMI to direct self-assemble PS-b-PMMA systems of different molecular weights.

In the first approach, the process is based on the definition of the guiding patterns by means of EBL and subsequent functionalization by oxygen plasma, thus creating a chemical contrast on the surface strong enough to guide the BCP self-assembly. This process has been successfully implemented to three PS-b-PMMA systems with different polymer chain lengths. First, the process has been demonstrated for guiding stripes of half $L_0$ widths, and then for wider guiding stripes with $(n + 1/2) \cdot L_0$ widths. This has allowed to relax the lithography requirements in terms of resolution, enabling the process integration to smaller PS-b-PMMA and high-$\chi$ materials.

Furthermore, an extensive characterization of the chemical guiding pattern has been performed in order to define the role of the interface energies between the substrate and the BCP domains. To do so, a novel experimental method by using homopolymer blends has been designed to determine the contact angle between the homopolymers in the blend, and thus calculate the difference on surface free energies by using Young’s equation. This characterization has led to the conclusion that the main driving force in a chemical epitaxy process comes from the chemical interactions taking place at the surface. Moreover, it has been demonstrated that depending on the BCP system there is the need of a specific set of interface energies which are given by the brush layer and BCP annealing conditions.

On the other hand, the definition of the contact angles has been used to implement the experimental data on a DSA model and simulate a specific chemical epitaxy process. From the simulation results, it can be concluded that a good correlation between the experimental DSA process and the one predicted by the theory has been demonstrated. On the other hand, it has been found out that the responsiveness of the brush layer plays a very important role on the self-assembly process, favoring the standing lamellae when using an intermediate or low brush density, due to the interdigitation between it and the BCP domains.

In the two last chemical epitaxy approaches, the chemical guiding patterns have been defined directly on the brush thus avoiding the use of resists. These novel methods present the advantage of simplifying the processing sequence by reducing the number of single processing steps.

On the first direct writing method, the guiding patterns are created by means of EBL, and it has been demonstrated that the feature dimensions can be accurately controlled by varying the e-beam dose using a much simpler processing as compared to other methods reported in the literature. On the second approach, the guiding patterns are created by
locally oxidation of the surface with AFM nanolithography. This method, as compared with EBL direct writing, presents the advantage of the unique resolution performance of AFM.

Nevertheless, the major drawback of both methods is the low throughput arising from the limited writing speed which at present limits their industrial application. In any case, the creation of guiding patterns either by AFM or direct writing EBL can be considered as simple and affordable methods to study the alignment behavior of BCPs.

Further characterization by X-ray techniques of the different chemical guiding patterns is presented in *chapter 6*. 
3. Directed self-assembly of PS-b-PMMA block copolymers by chemical epitaxy

3.8. References


3. Directed self-assembly of PS-b-PMMA block copolymers by chemical epitaxy


Chapter 4

Directed self-assembly of PS-\textit{b}-PMMA block copolymers by graphoepitaxy

Graphoepitaxy generates topographical structures that guide the self-assembly of BCPs. It is well known that in order to obtain an optimal BCP alignment, not only the topographical guiding pattern specifications have to be taken into account, but also the chemical interactions between the block copolymer domains and the topographical pattern (bottom and walls).

In this chapter, the implementation, optimization and characterization of a graphoepitaxy process for PS-\textit{b}-PMMA is presented. The definition of the guiding patterns is introduced first, using e-beam lithography, and then by photolithography to demonstrate a simpler and less time-consuming process.

On the other hand, an experimental demonstration to control the orientation of the block copolymer depending on the surface affinities is presented.
4.1. Introduction to directed self-assembly of block copolymers by graphoepitaxy

Self-assembly of BCPs exhibits random domain orientation, as already shown in previous sections. It limits their applicability, and therefore, topographical or chemical guiding patterns are used to guide the nanostructures and overcome such random distribution.\textsuperscript{1-3} While chapter 3 is focused on the description and characterization of the different implemented chemical epitaxy processes, the present chapter aims to briefly discuss about the graphoepitaxy approach to guide BCPs, including the influence of topographical surfaces on DSA and the different ways to control the BCP orientation.

Graphoepitaxy consists in creating topographical features on the substrate to enforce the self-assembly of BCPs, thus enhancing the lateral order on the BCP microdomains.\textsuperscript{4-8} However, not only the commensurability has to be taken into account, but also the interfacial interactions between the substrate and the polymer, as well as substrate roughness. The first graphoepitaxy DSA process was introduced by Kramer et al. in 2001, and it is schematized below in Figure 4.1.\textsuperscript{9}

![Figure 4.1. Scheme of the overall graphoepitaxy process developed by Kramer et al. using topographical guiding patterns to direct BCP self-assembly\textsuperscript{9}](image)

After the creation of the topographical pre-pattern, the brush is deposited to control the BCP affinity, and then the BCP fills the topographical regions confining the BCP. Normally, the distances filled by the BCP are larger than $L_0$, thus achieving high density multiplication factors. This means that the effective pitch of the patterning is considerably reduced, thus relaxing the lithography step in terms of resolution.

There are different methodologies to create the guiding patterns, all of them based on the use of a top-down approach. The most commonly used technique is photolithography\textsuperscript{4,6,9,10}, but also IL\textsuperscript{11-13} or EBL\textsuperscript{14-16} are used. An alternative method to create the guiding patterns is by using a NIL template into a resist rather than on the substrate.\textsuperscript{17}

As discussed in chapter 1, in photolithography, the guiding pattern size is limited by the wavelength and the lens numerical aperture (when using 193 nm wavelength, the minimum pattern size is limited to 37 nm)\textsuperscript{18}, whereas in IL shorter wavelengths can be used, thus
increasing the photolithography resolution. It has been demonstrated that resolutions below 10 nm when using EUV light of wavelength 13.5 nm, have been obtained.\textsuperscript{19,20} Nevertheless, compared with the high equipment cost and process complexity of IL, photolithography presents the added benefit of being a rapid and easy lithography process.

On the other hand, EBL offers resolutions below 10 nm, determined by the voltage, beam spot size, resist and e-beam dose.\textsuperscript{21} Despite having lower throughput as compared to the other two lithographic techniques, EBL does not require the use of a photomask. On the other hand, as compared with the last two discussed methods, it presents the advantage of fabricating less LER trenches, thus enabling the applicability of the process for smaller BCPs.

As it has been previously discussed, graphoepitaxy DSA is rather simple and cost-effective approach. However, it has the limitation of requiring a minimum trench width to have order in the self-assembly process. This implies a compromise in the storage space for being used in bit patterned media fabrication.\textsuperscript{22,23} To solve this problem, the use of shallow features to control BCP ordering has been demonstrated, and first introduced by Park et al.\textsuperscript{24}

In the mentioned work, described in Figure 4.2, single crystalline wafers of silicon with a given miscut orientation are used. Upon thermal annealing an atomic-scale periodic topography over the substrate is generated. Then the BCP is guided by the confinement effect of the planes. Nevertheless, the precise alignment of the BCP does not occur since the BCP period is normally not commensurate with the underlying guiding pattern period.

![Figure 4.2. Schematic representation of graphoepitaxy process using the strategy developed by Parker et al. of creating patterns based on highly oriented crystalline facets on a single crystal surface\textsuperscript{24}](image)

Normally topographical guiding patterns are created on hard-substrates which present the inconvenient of remaining after pattern transfer, being undesirable for device fabrication. Recently, there have been presented other graphoepitaxy approaches where organic pre-patterns are used.\textsuperscript{25-27} This novel approach was introduced in 2009 by Jeong et al. in which they used an organic negative-tone photoresist to create the guiding patterns.\textsuperscript{26}
4.2. Development and implementation of graphoepitaxy on PS-b-PMMA by means of e-beam lithography

In graphoepitaxy DSA, the geometry of the guiding pattern plays a key role during the process. Nevertheless, as in chemical epitaxy, there is also need to control the interfacial interactions of the substrate (bottom and walls) with the BCP. This interaction is normally controlled with the use of random copolymers to generate a neutral surface, and with the BCP processing conditions.

On the other hand, it is also important to consider the defectivity of the process with respect to the guiding pattern dimensions. It has been demonstrated that, as the separation between trenches grow larger, defect density increases\(^\text{9,28}\). Furthermore, the lateral order on edges presents less defectivity compared to the middle of the trench, when trench widths are larger\(^\text{4,29,30}\).

4.2.1. Materials and methods

4.2.1.1. Description of the graphoepitaxy process

The technique implemented at IMB-CNMI to direct self-assemble PS-b-PMMA and high-\(\chi\) BCPs, is depicted in Figure 4.3. It consists of 6-steps: (i) e-beam writing on PMMA resist, (ii) PMMA development, (iii) silicon etching, (iv) resist removal, (v) polymer brush grafting on silicon, and (vi) BCP spin-coating.

![Diagram of the graphoepitaxy process](image)

**Figure 4.3.** Schematic of the graphoepitaxy process for PS-b-PMMA by means of e-beam lithography

4.2.1.2. Brush and block copolymer materials

Lamellae PS-b-PMMA of 22 nm pitch has been used for the DSA process, with a PS\(_{50}\)-r-PMMA brush, processed under different conditions depending on the final desired structure. The specifications of brush and BCP material are depicted in Table 4.1.

| Table 4.1. Specifications of brush and BCP used for graphoepitaxy DSA |
|-----------------------------|---------------------|--------|------------------|
| Material                    | Molecular weight    | PDI    | Pitch (SEM)      |
| PS\(_{50}\)-r-PMMA          | 7.9 kg/mol          | 1.85   | -                |
| PS-b-PMMA                   | 42.3 kg/mol         | 1.10   | 22.5 nm          |
4. Directed self-assembly of PS-b-PMMA block copolymers by graphoepitaxy

4.2.1.3. Creation of the topographical guiding patterns

The aim of using graphoepitaxy is to, later on, obtain a novel class of nanowires based mechanical resonators (chapter 7). It is depicted in Figure 4.4. The fabrication process of the mechanical resonators will be based on the use of graphoepitaxy DSA and therefore, there is a need to study first the DSA process.

The guiding patterns designed to study the DSA graphoepitaxy process are those which will be used at a later stage to fabricate the mechanical resonators. These are first defined by EBL in order to demonstrate the applicability of the process, and then by photolithography in order to validate a possible industrial scalability.

![Figure 4.4](image.png)

**Figure 4.4.** Schematic representation of a device based on an array of identical nanobeams made by directed self-assembly of block copolymers

The starting substrates are 0.9 x 0.9 cm² chips bearing a native silicon oxide layer (\{100\}, p-type silicon wafers of 4-40 Ω·cm resistivity). Previously to the lithography process, the sample surface is cleaned and activated by an oxygen plasma for 10 min at 500 W and 50 sccm of oxygen flow.

Figure 4.5 shows the pattern designs used to create the guiding patterns with a negative-tone resist. It consists of two 10 x 10 μm² pads separated from each other a w distance. In the different designs, the length of the guiding patterns has been kept constant, and then the w has been varied from 60 nm to 1 μm. This wide range has been selected in order to, later on, reproduce the results by using photolithography in which the minimum resolution is 350 nm.

![Figure 4.5](image.png)

**Figure 4.5.** Schematic representation of the design used to study the PS-b-PMMA DSA by graphoepitaxy

120
After the substrate cleaning process, a negative-tone resist, AR-N7500-08, is spin-coated on the top of the silicon at 4000 rpm for 1 min, and annealed at 85°C for one further min, to get a 150 nm thick film. Then, the guiding patterns are defined by EBL in a RAITH 150Two equipment. The exposure has been performed at 20 kV and 110 pA beam current, with a nominal beam diameter of 2 nm. The exposure has been defined with the designs depicted in Figure 4.5 with an e-beam dose of 150 μC/cm². The writing speed has been, therefore 7.33 m/s by using a line step of 10 nm.

Once the exposure has been completed, the samples are developed by using the resist developer AR-300-47. The samples are dipped into the developer for 2 min, and then into water for two further minutes. Finally, the samples are annealed at 135°C for 5 min.

To finally define the topographic guiding patterns, a silicon etching of 120 nm is performed on the surface by using the negative-tone resist as a mask. The silicon etching conditions are depicted in Table 4.2.

Table 4.2. RIE conditions for silicon etching

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>[SF₆] (sccm)</td>
<td>35</td>
</tr>
<tr>
<td>[C₃F₅] (sccm)</td>
<td>45</td>
</tr>
<tr>
<td>Power Source (W)</td>
<td>100</td>
</tr>
<tr>
<td>Chuck Power (W)</td>
<td>20</td>
</tr>
<tr>
<td>Time (s)</td>
<td>40</td>
</tr>
<tr>
<td>Pressure (Pa)</td>
<td>2</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>20</td>
</tr>
<tr>
<td>Silicon etched</td>
<td>120</td>
</tr>
</tbody>
</table>

Figure 4.6 shows a SEM image of the guiding patterns after having etched 120 nm of silicon. In the image, 100 nm of resist are still present. It is removed by exposing the sample to oxygen plasma at 500 W for 10 min with an oxygen flow of 50 sccm, prior to BCP spin-coating.

![SEM image of the guiding pattern](image)

**Figure 4.6.** SEM cross-section image of the graphoepitaxy guiding pattern created by e-beam lithography after silicon etching
4.2.1.4. Deposition of the brush layer

As previously discussed, for the fabrication of the mechanical resonators, a perpendicular oriented BCP morphology is required. Therefore, in order to avoid the parallel oriented morphology, both the bottom and the walls of the guiding pattern need to have neutral affinity for the BCP.

Depending on the brush solution concentration and spin-coating speed, the brush grafting can be controlled (Figure 4.7). If the brush solution is diluted and it is spin-coated at very high spin speeds, its grafting occurs only at the bottom of the guiding patterns (Figure 4.7.a). This means that the bottom of the guiding pattern presents a neutral affinity for both BCP domains, whereas the walls (silicon is not grafted) are more PMMA affine. On the other hand, if the brush concentration is increased, it is grafted in the whole silicon surface, thus presenting neutrality in both surfaces (Figure 4.7.b).

![Figure 4.7. Schematics of graphoepitaxy patterns with brush (a) only at the bottom and (b) at the bottom and walls](image)

As discussed above, the desired situation is the one depicted in Figure 4.7.b. Therefore, a 2% PS_{800k-r-PMMA} at 1500 rpm is spin-coated on the top of the guiding patterns and consequently annealed at 230°C for 5 min in a nitrogen environment. Then, the non-grafted brush is removed by dipping the sample in PGMEA for 5 min at 40°C in an ultrasonic bath. Finally, a 0.5% PS-b-PMMA solution is spin-coated at 2500 rpm and annealed at 230°C for 10 min under a nitrogen flow to promote the BCP self-assembly.

4.2.2. Directed self-assembly by graphoepitaxy of PS-b-PMMA results

The DSA experiments have been performed for PS-b-PMMA of 22 nm pitch on topographical guiding patterns by varying their separation width. The separation range width has been studied between 60 nm and 1 μm. It has to be pointed out, that after the BCP deposition, the solution tends to go inside the trenches due to the topographical confinement effect. Therefore, the defectivity on edges is strongly reduced, as compared with the middle of the trench when its width is larger, or with the rest of the sample.4,29,30

Figure 4.8 shows the SEM images of the corresponding DSA process when using different separation widths. It can be observed that the maximum separation width at which the
BCP shows a perpendicular orientation with respect to the guiding patterns is between 500 nm and 600 nm.

![Figure 4.8. PS-b-PMMA (L₀ = 22 nm) DSA by graphoepitaxy by using separation widths of (a) 100 nm, (b) 160 nm, (c) 250 nm, (d) 400 nm, (e) 500 nm and (f) 600 nm](image)

Above 600 nm separation width, the orientation is no longer maintained, and areas without BCP start to appear. Figure 4.9 shows the DSA defects which appear in guiding patterns above 700 nm separation width.

![Figure 4.9. PS-b-PMMA (L₀ = 22 nm) DSA by graphoepitaxy by using separation widths of (a) 700 nm, (b) 900 nm and (c) 1 μm](image)

As previously discussed, the BCP tends to go inside the trenches due to the topographical confinement effect. It is observed in the SEM image of Figure 4.10. In the zoom-in image, it is observed that the BCP dewets outside the guiding pattern, whereas inside the guiding pattern presents a well-ordered thick structure. This is in agreement with some works, which demonstrate that the wider the trench separation, the highest the defectivity on the middle of the confinement or outside the guiding pattern, as compared to the lateral order on the trench edges.⁴,²⁹,³⁰
4.3. Development and implementation of graphoepitaxy on PS-\(b\)-PMMA by means of photolithography

The graphoepitaxy process has been successfully implemented at IMB-CNAM for guiding trench widths up to 600 nm. Therefore, the guiding patterns can be easily defined by means of photolithography since its critical dimension is 350 nm. Hence, the graphoepitaxy process gains more interest, since it presents the added advantages of being a low-cost and time-saving approach.

To define the guiding patterns by means of photolithography, it is necessary first to design and fabricate a photomask. The desired designs for the mask are computerized in a data file. Then, this data is converted to a series of features, and written onto a quartz substrate covered with a layer of chromium. The features are normally written by an e-beam writer on the mask surface. Finally, after the e-beam lithography, the exposed chromium is etched away, leaving the exposed features free in order to let the illumination light system go through.

4.3.1. Materials and methods

4.3.1.1. Description of the graphoepitaxy process

The graphoepitaxy process using photolithography is depicted in Figure 4.11. As observed, the processing steps are the same, being the only differences the materials used to perform the photolithography, and the starting substrates.
4. Directed self-assembly of PS-b-PMMA block copolymers by graphoepitaxy

1. Photolithography

2. PMMA development + Si etching

3. Resist stripping + Brush spin-coating

4. BCP spin-coating

Figure 4.11. Schematic of the graphoepitaxy process for PS-b-PMMA by means of photolithography

4.3.1.2. Creation of the topographical guiding patterns

In order to define the topographical patterns into the substrate, the first step consists in the fabrication of the photomask. The software that has been used to define the mask designs is Cadence.

The projected reticle presents four quarters (Q1 to Q4) defined with different device designs, in order to use it, not only for DSA, but for other applications. The first area Q1 is depicted in Figure 4.12.

As observed, it consists of an array of features grouped in four identical devices. Then, the length of the trenches and the separation width are varied in columns and rows, respectively. Trench lengths up to 40 μm, and separation widths up to 1 μm have been designed. The dimensions of the guiding patterns for this first quarter are defined in Table 4.3.

Figure 4.12. Schematic representation of the Q1 area of the reticle used for the photolithography
Table 4.3. Specifications of the geometrical dimensions of Q1 designs as a function of the trench length and separation width

<table>
<thead>
<tr>
<th>L (µm)</th>
<th>0</th>
<th>350</th>
<th>400</th>
<th>450</th>
<th>500</th>
<th>550</th>
<th>600</th>
<th>650</th>
<th>700</th>
<th>750</th>
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<th>850</th>
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<tr>
<td>2</td>
<td>A1</td>
<td>A2</td>
<td>A3</td>
<td>A4</td>
<td>A5</td>
<td>A6</td>
<td>A7</td>
<td>A8</td>
<td>A9</td>
<td>A10</td>
<td>A11</td>
<td>A12</td>
<td>A13</td>
<td>A15</td>
<td>A15</td>
</tr>
<tr>
<td>5</td>
<td>B1</td>
<td>B2</td>
<td>B3</td>
<td>B4</td>
<td>B5</td>
<td>B6</td>
<td>B7</td>
<td>B8</td>
<td>B9</td>
<td>B10</td>
<td>B11</td>
<td>B12</td>
<td>B13</td>
<td>B14</td>
<td>B15</td>
</tr>
<tr>
<td>10</td>
<td>C1</td>
<td>C2</td>
<td>C3</td>
<td>C4</td>
<td>C5</td>
<td>C6</td>
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<td>C9</td>
<td>C10</td>
<td>C11</td>
<td>C12</td>
<td>C13</td>
<td>C14</td>
<td>C15</td>
</tr>
<tr>
<td>20</td>
<td>D1</td>
<td>D2</td>
<td>D3</td>
<td>D4</td>
<td>D5</td>
<td>D6</td>
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<td>E4</td>
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<td>E7</td>
<td>E8</td>
<td>E9</td>
<td>E10</td>
<td>E11</td>
<td>E12</td>
<td>E13</td>
<td>E14</td>
<td>E15</td>
</tr>
</tbody>
</table>

For further applications on the field, other designs have been defined (Q2 and Q3 depicted in Figure 4.13 and Figure 4.14, respectively).

Designs Q2 are formed of groups of two identical devices defined in three columns by varying $L = 2, 5$ and 10 µm, and in 15 rows by varying $w$ up to 1 µm.

![Figure 4.13. Schematic representation of the Q2 area of the reticle used for the photolithography](image)

Areas Q3 (Figure 4.14), represent more complex designs. On the one hand, in the first two columns (Figure 4.14.a) there are two identical devices with different trench lengths each one ($L = 5, 10, 20$ and 30 µm) repeated in row by varying the separation width, $w$, up to 1 µm. On the other hand, in the third column (Figure 4.14.b) devices in which each one presents different trench lengths ($L = 5, 10, 20$ and 30 µm) with three and four gaps in each side, separated a $w$ distance, are represented. As for the previous designs, the separation width is varied in row, up to 1 µm.
4. Directed self-assembly of PS-b-PMMA block copolymers by graphoepitaxy

Figure 4.14. Schematic representation of the Q3 area of the reticle used for the photolithography

In the last quarter, Q4, squares, arrays of trenches or circles are defined (Figure 4.15).

Figure 4.15. Schematic representation of the Q4 area of the reticle used for the photolithography

The starting substrates are 4 inch silicon wafers bearing a native silicon oxide layer (\{100\}, p-type silicon wafers of 4-40 Ω · cm resistivity). Previously to the photolithography process, 600 nm of a positive-tone resist, OIR 620-09, are deposited and annealed at 100°C for 30 s on an automatic coater-developer system, GAMMA80 Süss.

The photolithography is performed on a stepper i-line, NSR 2205i12D equipment, which has a critical dimension of 350 nm and a maximum exposure area of 22 x 22 mm². The exposure time is 535 ms with a focus of -0.5 μm. Then, the wafer is developed by TMAH for 28 s, and annealed at 115°C for 30 s in a hot-plate.

Once the wafers have been exposed and developed, the topographical patterns are finally defined by performing a silicon etching in DRIE ALCATEL 601E equipment by using the
same conditions of Table 4.2. Figure 4.16 shows a SEM images of how the guiding patterns look like after silicon etching.

![SEM cross-section image of the graphoepitaxy guiding pattern created by photolithography after silicon etching](image)

**Figure 4.16.** SEM cross-section image of the graphoepitaxy guiding pattern created by photolithography after silicon etching

Afterwards, the wafer is cut into small samples (1 x 1 cm²), and the brush layer is deposited and annealed as performed in section 4.2.1.4.

### 4.3.2. Directed self-assembly by graphoepitaxy results

The DSA experiments have been performed by using the same PS-\(b\)-PMMA of 22 nm pitch and processing conditions that had been used for the later approach. Figure 4.17 shows the results of the DSA graphoepitaxy process, when the guiding patterns have been defined by photolithography. As observed in the images, the BCP self-assembly behavior is the same as the one shown in Figure 4.8, where the guiding patterns were created by EBL. The maximum trench separation width in which no defects are observed is 750 nm (Figure 4.17.e).

![PS-\(b\)-PMMA (\(L_o = 22\) nm) DSA by graphoepitaxy by using separation widths of (a) 450 nm, (b) 500 nm, (c) 650 nm, (d) 700 nm, (e) 750 nm and (f) 850 nm](image)

**Figure 4.17.** PS-\(b\)-PMMA (\(L_o = 22\) nm) DSA by graphoepitaxy by using separation widths of (a) 450 nm, (b) 500 nm, (c) 650 nm, (d) 700 nm, (e) 750 nm and (f) 850 nm
It is therefore demonstrated, that the presented graphoepitaxy approach can be easily simplified in terms of cost and time, by using a photolithography step instead of EBL. Furthermore, the DSA has been demonstrated, and will be the basis for the design and fabrication of the nanomechanical resonators in chapter 7.

4.4. Surface affinity control on topographical guiding patterns

The DSA process by graphoepitaxy is not only governed by the topographical guiding patterns, but also by the affinities toward the underlying substrate. In order to demonstrate the control on the BCP orientation depending on the substrate conditions, two DSA experiments have been performed by varying the substrate conditions in order to force the BCP to be aligned perpendicular and parallel to the substrate, respectively.

The guiding patterns have been created by IL in collaboration with the Molecular Foundry. The starting substrates have been bare silicon and silicon with an 80 nm thick antireflective layer on top. Figure 4.18 shows a schematic representation of both guiding patterns. The dimensions of the trenches are 200 nm width and 80 nm height, they are separated 500 nm from each other.

![Figure 4.18. Graphoepitaxy guiding patterns made of (a) silicon and (b) silicon + ARC](image)

Prior to brush deposition, both guiding patterns are cleaned, and the resist is removed by dipping the sample into hot acetone (40°C) for 5 min in an ultrasonic bath and into IPA for 5 more minutes. Then, a 2% PS<sub>90K</sub>-r-PMMA brush solution is deposited on the top of the guiding patterns at the same spin-speed (2000 rpm), in order to coat the whole sample surface as depicted in Figure 4.7.

After removing the non-grafted brush by rinsing the samples with PGMEA for 5 minutes in an ultrasonic bath at 40°C, a 1.5% PS-<i>b</i>-PMMA of 22 nm pitch is spin-coated on the top of the guiding patterns at 2000 rpm, and annealed at 230°C for 10 min.

Figure 4.19 shows the results of the DSA graphoepitaxy process on silicon (Figure 4.19.a) and on silicon + ARC (Figure 4.19.b) guiding patterns. As observed in the images, despite using the same processing conditions and materials, the orientation of the BCP is different depending on the substrate of the guiding patterns.
Figure 4.19. PS-b-PMMA ($L_0 = 22$ nm) DSA by graphoepitaxy on (a) silicon and (b) silicon + ARC guiding patterns.

The difference on the BCP orientation occurs because the brush layer does not graft onto the ARC layer walls, since it is a carbon-based material. Therefore, in the case where the patterns are created on silicon + ARC, the brush is only present at the bottom, and therefore the walls do not present a neutral affinity as they do in the samples where the guiding patterns are made of silicon.

Figure 4.20 illustrates the DSA process in each situation. When the guiding patterns are made of silicon (Figure 4.20.a), the brush is grafted on the whole silicon surface, promoting a neutral affinity for both BCP domains at the walls and at the bottom of the trenches. Therefore, the BCP is oriented perpendicular to the trench orientation. On the other hand, when the guiding patterns are made of silicon + ARC (Figure 4.20.b), the brush is only grafted at the bottom of the patterns, promoting there a neutral affinity, whereas the walls are PMMA attractive. In consequence, the BCP tends to be orientated parallel to the trenches.

Figure 4.20. Schematic representation of the DSA by graphoepitaxy process when using (a) silicon and (b) silicon + ARC guiding patterns

As observed in Figure 4.19.b, the density multiplication factor achieved is 11$L_0$, which is much more than it has been demonstrated for lamellar PS-b-PMMA system. For this system, in order to demonstrate that the BCP domains have the perpendicular morphology through the film thickness down to the substrate, the cross-section of the guiding patterns
has been characterized. To carry out the inspection, the PMMA has been first removed by using soft oxygen plasma at 260W with an oxygen flow of 50 sccm for 18 s.

Figure 4.21 shows the SEM cross-section of the guiding pattern, after removal of the PMMA domain. The cross-section has been obtained by the cleavage of the sample. As it is observed, the brush presents a neutral affinity to both domains of the BCP since the perpendicular morphology is maintained through the film.

**Figure 4.21.** SEM cross-section of PS-b-PMMA ($L_0 = 22$ nm) DSA by graphoepitaxy on *silicon* + *ARC* guiding patterns.
4.5. Summary and conclusions

A graphoepitaxy approach to guide the self-assembly of PS-\(b\)-PMMA BCPs has been presented. Such approach has been designed in order to implement the fabrication of nanowires based on nanomechanical resonators (\textit{chapter 7}).

The guiding patterns have been defined first by e-beam writing in order to demonstrate the viability of the process. Once it has been proved and optimized, the samples have been created at 4 inch wafer scale, and the guiding patterns have been designed by means of photolithography with a critical dimension of 350 nm. From the DSA results, it has been observed, that the BCP shows a good alignment behavior with trench separation widths up to 600 nm, but such alignment is lost at larger widths. Moreover, as reported in the literature, it has been seen that the larger the width of the trenches, the higher the BCP defectivity, being it significantly increased in the center of the trenches.

On the other hand, a way to control the BCP orientation as a function of the substrate used has been demonstrated. Depending on the chemical affinities between the substrate (both walls and bottom) and the BCP domains, the orientation can be parallel or perpendicular to the trench direction.

This graphoepitaxy approach will be later on implemented on high-\(\chi\) BCP systems (\textit{chapter 5}), by adding an alternative step to enhance the process and adapt it to other chemistries.
4.6. References


Chapter 5

Directed self-assembly of high-$\chi$ block copolymers

The increasing demand on the fabrication of ever-smaller structures requires a continuous decrease in the feature size of device components. PS-b-PMMA has a limit in its feature size around 12 nm due to its low $\chi$ value. Therefore, BCPs with larger $\chi$ values which provide sub-10 nm resolution have to be explored, demonstrating a controlled synthesis and good etching selectivity.

In this chapter, the self-assembly of two high-$\chi$ systems is studied and characterized. Then, its implementation to the developed directed self-assembly processes for PS-b-PMMA is also described. Moreover, a novel approach based on a combination technique between chemical and graphoepitaxy is presented, achieving high density multiplication factors.
5.1. Introduction to high-χ block copolymers

DSA based high-χ BCPs offer a complementary solution to conventional DUV or EUV lithography, allowing getting resolutions below 10 nm at a more affordable cost. In general, low-χ BCPs tend to be easier to anneal since the movement of polymer domains encounters lower activation barriers. However, high-χ BCPs are more difficult to direct and orientate by thermal annealing due to the different properties between blocks. Normally, they need an extra top-coat layer or the use of solvent annealing to obtain the perpendicular morphology, which increases processing costs and further complicate an already complex process.

In this chapter, the implementation of chemical epitaxy process based on EBL and subsequent substrate functionalization has been implemented for two different lamellar systems which exhibit a moderate Flory-Huggins parameter, yet higher, than PS-b-PMMA: PS-b-PLA\(^{17}\) and poly(dimethylsiloxane)-b-poly(lactic acid) (PLA-b-PDMS-b-PLA).\(^{8,11}\) In particular for these two BCP systems, the synthesis of random copolymers is not trivial and has not been reported in the literature. In addition, neutral layers containing silicon complicate the step of transferring the features to the substrate. Therefore, in order to tune the surface energy between the high-χ system and the substrate, the influence of different random PS-r-PMMA copolymers with different compositions has been investigated.

5.2. PS-b-PLA systems

5.2.1. PS-b-PLA synthesis

PS-b-PLA is based on the modification of the common PS-b-PMMA system in which the PMMA domains are replaced by another block which allows tuning the Flory-Huggins parameter between the two blocks. It exhibits a moderate but higher Flory-Huggins parameter, as compared with PS-b-PMMA (χ = 0.23 at 298K).\(^{12}\) Moreover, this BCP system has shown the availability to self-assemble under thermal treatments\(^{13}\), avoiding thus the use of complex solvent annealing treatments which increment the processing costs.

The BCP synthesis was performed at the Laboratoire de Chimie des Polymères Organiques (LCPO) and Arkema. Targeted structures were designed in order to obtain BCPs with overall molecular weight in number, \(M_n\), and dispersity index, \(PDI\), lower than 15 kg/mol and 1.25, respectively, which lead to sub-10 nm lithographic structures. Figure 5.1 shows the two-step synthetic pathway for the synthesis of PS-b-PLA. The synthesis of monofunctionalized precursor blocks with predefined molecular weights was performed leading to hydroxyl terminated PS. The controlled growing of the PLA block was then achieved by
using these PS blocks as macroinitiators and by using triazabicyclodecene (TBD) as catalyst for the reaction, thus avoiding the use of non-organic catalysts during synthesis, which simplifies the metallic purification step. The control of the conversion of the PLA growing chains allows the formation of PS-b-PLA BCPs with various compositions.

In order to determine the molecular weight of PS domains, Size Exclusion Chromatography (SEC) as well as $^1$H Nuclear Magnetic Resonance spectroscopy (NMR) have been used. The obtained results are summarized in Table 5.1. On the other hand, the BCP morphology was determined by small angle X-ray scattering (SAXS).

![Synthetic pathway used for the synthesis of PS-b-PLA](image)

**Figure 5.1.** Synthetic pathway used for the synthesis of PS-b-PLA

**Table 5.1.** Macromolecular specifications of PS-b-PLA BCP. Macroinitiator $M_n$ was determined by SEC using PS standards, BCP $M_n$ and volume fraction by $^1$H-NMR, PDI by SEC in THF and the morphology by SAXS

<table>
<thead>
<tr>
<th>Macroin. $M_n$ (kg/mol)</th>
<th>BCP $M_n$ (kg/mol)</th>
<th>PDI</th>
<th>Volume fraction</th>
<th>Morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.6</td>
<td>10.8</td>
<td>1.10</td>
<td>0.48/0.52</td>
<td>Lamellae</td>
</tr>
</tbody>
</table>

### 5.2.2. PS-b-PLA self-assembly

In order to control the self-assembly in thin film configuration, the use of random copolymers grafted onto the substrate is also used since it allows controlling the surface energy between the BCP domains and the substrate. Nevertheless, the synthesis of random copolymers different from PS-$r$-PMMA is not well-established, and it has not been reported in the literature yet.

Therefore, different processing parameters have been studied in order to get the perpendicular lamellae with fingerprint morphology on free-surface, including annealing processing conditions, BCP film thickness and brush layer material. In particular, four brush polymers based on PS-$r$-PMMA have been used by varying the composition of PS. The specifications of these materials are summarized in Table 5.2.

**Table 5.2.** PS-$r$-PMMA brush layer specifications

<table>
<thead>
<tr>
<th>Brush material</th>
<th>$M_n$ (kg/mol)</th>
<th>PDI</th>
<th>PS Volume fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-OH</td>
<td>14.5</td>
<td>1.4</td>
<td>1</td>
</tr>
<tr>
<td>PS$_{60/40}$-$r$-PMMA</td>
<td>7.9</td>
<td>1.85</td>
<td>0.59</td>
</tr>
<tr>
<td>PS$_{40/60}$-$r$-PMMA</td>
<td>9.9</td>
<td>1.34</td>
<td>0.70</td>
</tr>
<tr>
<td>PS$_{85/15}$-$r$-PMMA</td>
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<td>1.46</td>
<td>0.48</td>
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</tbody>
</table>
For each of these brush materials, an annealing temperature range between 100 and 230°C has been used, with annealing times from 10 min to 24 h under a free-oxygen environment. On the other hand, for each situation, a broad study of the BCP self-assembly behavior depending on film thickness has been also conducted.

Figure 5.2 shows a SEM image of PS-b-PLA self-assembly with the optimal processing conditions found. The perpendicular morphology has been obtained when using PS-r-PMMA with 48% PS content annealed at 230°C for 5 min and with a BCP film thickness of 23.5 nm (1.2L₀) annealed at 100°C for 24 h under vacuum conditions. Due to the χ variations with temperature, it is necessary to work at a temperature near to 100°C, which is very close to PS glass transition temperature.

![Figure 5.2](image)

**Figure 5.2.** SEM image of lamellar PS-b-PLA self-assembly for a film thickness of 23.5 nm annealed at 100°C for 24 h under vacuum on top of PS₈₅₇-r-PMMA.

Figure 5.3 shows PS-b-PLA self-assembly behavior depending on the content of PS brush layer (the annealing conditions and BCP film thickness are the ones described in Figure 5.2). It is observed that as the PS brush content decreases, the interfacial energies between PS and PLA with the surface become more similar since perpendicular lamellae appear on the surface. When PS₈₅₇-r-PMMA is used, both interface energies are balanced and thus induce the fingerprint BCP morphology along the sample. As observed, the BCP morphology strongly depends on the brush material composition.

![Figure 5.3](image)

**Figure 5.3.** SEM images of lamellar PS-b-PLA self-assembly for a film thickness of 23.5 nm annealed at 100°C for 24 h under vacuum on top of different PS-r-PMMA.

On the other hand, Figure 5.4 shows the morphology the BCP takes depending on its film thickness when using PS₈₅₇-r-PMMA as a brush (the annealing conditions are described in Figure 5.2). It is clearly observed that the morphology is very sensitive to film thickness variations, and thus an accurate film thickness control has to be taken into account for DSA chemical epitaxy processes.
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Figure 5.4. SEM images of lamellar PS-b-PLA self-assembly annealed at 100°C for 24 h under vacuum on top of PS$_{ST-r}$-PMMA by varying the BCP film thickness.

The BCP pitch has been also analyzed by AFM characterization (Figure 5.5). From the Fast Fourier Transform (FFT) image characterization it is observed that the pitch is 21 nm.

![AFM characterization of PS-b-PLA self-assembled structures](image)

Figure 5.5. AFM characterization of PS-b-PLA self-assembled structures under the optimal self-assembly conditions found. The obtained pitch is 21 nm.

From the study performed on the PS-b-PLA self-assembly on free-surface, it can be concluded that a surface which balances the interface free energies between the domains and the surface has been found, thus allowing to obtain the perpendicular morphology in large areas when using a thermal treatment. Figure 5.2 suggests that PS$_{ST-r}$-PMMA is neutral to both domains of the BCP, thus balancing the free energies between the substrate and the blocks. In contrast, the perpendicular morphology is lost when other brush layers or non-commensurate film thickness are used.

On the other hand, since the BCP annealing time is too long for industrial applications, shorter annealing times have been tried by using a range temperature between 100 and 130°C in a N$_2$ environment, instead of in vacuum. The shorter annealing time leading to useful results, has been found for an annealing temperature and time of 100°C and 10 minutes, respectively. Figure 5.6 shows a comparison between PS-b-PLA self-assembly when it is annealed at the same temperature for 24h under vacuum and for 10 min with continuous nitrogen flow. Although it has been reported that PS-b-PLA requires large thermal annealing times to self-assemble$^{11}$, the obtained results demonstrate that is possible.
to dramatically reduce the thermal annealing times enabling the process to be suitable for an industrial application.

![Figure 5.6. SEM images of lamellar PS-b-PLA self-assembly annealed at (a) 100°C under vacuum and (b) 100°C for 10 min in a N₂ environment.](image)

From the SEM images shown above, it can be observed that PS domains (brighter lines) are immersed in a PLA matrix (darker parts) which seem to be a little bit wider and with an irregular shape. Therefore, the BCP morphology of the film has been further investigated by adding a small amount of PS homopolymer to the PS-b-PLA solution. Figure 5.7 shows two PS-b-PLA SEM images before and after adding 5% of PS homopolymer. It is seen that after adding the small amount of PS, the brighter domains (PS blocks) become wider, and in consequence a more uniform line/space distribution is obtained. The solvent the BCP is dissolved in, presents higher selectivity to PLA domains.

![Figure 5.7. PS-b-PLA SEM images (a) before and (b) after adding 5% PS homopolymer.](image)

In order to explore the influence of the solvent, the PS-b-PLA self-assembly behavior has been also characterized as a function of the solvent. Apart from PGMEA, which is the solvent used for the later experiments, 1.5% toluene solution has also been tested. The study has been performed by using the same conditions which PS-b-PLA in PGMEA has shown the best self-assembly (PS<sub>50</sub>-r-PMMA brush, and 100°C for 24h in vacuum for the BCP annealing). Then, experiments as a function of the film thickness have been undertaken. From the characterization of SEM images of Figure 5.8, it can be noticed that the BCP pitch changes depending on which solvent it is dissolved in. It is also confirmed from the FFT AFM image characterization (Figure 5.9) which gives a pitch of 19.5 nm. This characterization has been also corroborated by GISAXS measurements, introduced in chapter 6.
This difference in the BCP pitch can be explained by the different solubility of the BCP with PGMEA and toluene. The selectivity of the solvents has been estimated using a solubility parameter study. The closer the solubility parameters of the solute and the solvent are, the larger the solubility will be. Hansen solubility parameters (HSP) developed by Charles M. Hansen in 1967, represent the total cohesive energy of a solvent or polymer separated in three terms: (i) dispersion, \( \delta_d \) (ii) polar, \( \delta_p \) and (iii) hydrogen bonding forces, \( \delta_h \):

\[
\delta^2 = \delta^2_d + \delta^2_p + \delta^2_h,
\]

(5.1)

To measure the similarity of the HSP of PLA and PS with the HSP of the solvent, the parameter \( R_a \) is introduced and defined as the distance between two molecules, representing a measure of how alike the polymer and the solvent are. Then, the smaller \( R_a \) the more likely they are to be compatible and the higher the swelling of the polymer:

\[
R^2_a = 4(\delta_{d1} - \delta_{d2})^2 + (\delta_{p1} - \delta_{p2})^2 + (\delta_{h1} - \delta_{h2})^2,
\]

(5.2)

The distance \( R_a \) can be compared to the solubility radius of the polymer, \( R_b \). The ratio between \( R_a \) and \( R_b \) is the relative energy difference (RED), of the system. If RED>1, then there is a low affinity between the polymer and solvent. If it is close or equal to one, the compound will partially dissolve. Table 5.3 shows the solubility parameters for the solvents and polymers involved in the process. From these values, the HSP distance between two molecules can be calculated and then the RED of the system which gives an idea of how suitable the solvent is for the system. Table 5.4 shows the RED calculated for toluene and PGMEA with respect to PS and PLA. From these values it can be concluded that PGMEA is more PLA selective, whereas toluene is nearly neutral with a slight selectivity to PS. Therefore, the different polymer-solvent solubility explains the variance on the BCP pitch. When the polymer is dissolved in PGMEA, it swells more PLA domains making them wider, whereas in toluene there is no swelling, and thus the copolymer pitch is reduced since it is almost neutral for both polymers.

![Figure 5.8. PS-b-PLA self-assembly as a function of film thickness when using (a) PGMEA, (b) toluene solutions](image)
5. Directed self-assembly of high-χ block copolymers

![Figure 5.9](image)

**Figure 5.9.** AFM characterization of PS-\(b\)-PLA self-assembled structures when using a toluene solution. The obtained pitch is 19.5 nm

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\delta_1) [MPa(^{-1/2})]</th>
<th>(\delta_\nu) [MPa(^{-1/2})]</th>
<th>(\delta_r) [MPa(^{1/2})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>18.0</td>
<td>1.4</td>
<td>2.0</td>
</tr>
<tr>
<td>PGMEA</td>
<td>15.6</td>
<td>5.6</td>
<td>9.8</td>
</tr>
<tr>
<td>PLA</td>
<td>18.6</td>
<td>9.9</td>
<td>6.0</td>
</tr>
<tr>
<td>PS</td>
<td>18.5</td>
<td>4.5</td>
<td>2.9</td>
</tr>
</tbody>
</table>

**Table 5.3.** Average solubility parameters for toluene, PGMEA, PLA and PS\(^6\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>RED(\text{PLA})</th>
<th>RED(\text{PS})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>0.849</td>
<td>0.422</td>
</tr>
<tr>
<td>PGMEA</td>
<td>0.621</td>
<td>1.135</td>
</tr>
</tbody>
</table>

**Table 5.4.** Relative energy difference calculated for toluene and PGMEA with respect to PS and PLA. PLA and PS radius are 10.7 and 8, respectively\(^{17}\)

### 5.2.3. PS-\(b\)-PLA directed self-assembly by chemical epitaxy

Once the self-assembly behavior on freesurface has been optimized, the chemical epitaxy process for PS-\(b\)-PMMA, presented in chapter 3, has been implemented to PS-\(b\)-PLA. The overall process is the same as the one depicted in Figure 3.2 from chapter 3, and the brush used is PS\(_{90}\%-r\)-PMMA. The guiding patterns have been designed for PS-\(b\)-PLA dimensions, and the oxygen plasma functionalization has been performed with the softer conditions available to not remove the brush but only slightly modify it, which makes the surface more attractive to PLA domains. A 1.5% BCP solution in PGMEA has been spin-coated at 4500 rpm (d = 23.5 nm) on top of the chemical guiding patterns and the sample has been annealed at 100°C for 24h under vacuum conditions.

Figure 5.10 shows a SEM image after PS-\(b\)-PLA DSA process when using a chemical guiding pattern of guiding stripes width equal to the BCP period and 4\(L_0\) pitch. A chemical contrast between guiding and background regions is observed, although the BCP has not been parallel oriented with respect to the guiding pattern but perpendicularly. On the other hand, and in contrast with PS-\(b\)-PMMA behavior, darker regions which correspond to modified areas have a strong affinity to the PLA blocks inducing the parallel morphology of the BCP.
Despite having tried several experiments in which the BCP film thickness, the annealing conditions and the BCP composition to change the orientation of the BCP domains with respect to the guiding pattern have been varied, no vertical orientation has been observed. Nevertheless, the DSA results show a considerable progress on high-χ BCPs, since it has been demonstrated a chemical epitaxy DSA in which the BCP has been treated with a thermal annealing instead of using the solvent annealing technique.\textsuperscript{18,2}

![Figure 5.10. SEM image of PS-b-PLA DSA for L_x = L_0 and 4L_0 pitch](image)

5.2.4. Experimental determination of surface free energy for PS-\textit{b-PLA} directed self-assembly

In order to chemically characterize the chemical interactions taking place in the DSA chemical epitaxy process of PS-\textit{b-PLA}, the same experimental methodology described in chapter 3 (Figure 3.14) to determine the surface free energies has been performed.

In the case of PS-\textit{b-PLA}, the chemical guiding patterns are performed on a PS_{b}\text{PS}\text{-}r-PMMA brush. Therefore, the contact angle of a PS/PLA 50:50 blend, has been determined on both modified and un-modified brush surfaces. Then, the difference of the surface free energy (\(\Delta \gamma_{\text{PS-brush}} - \Delta \gamma_{\text{PLA-brush}}\)) has been determined by using the Young’s equation (equation (3.1)). The interfacial tension between PS and PLA (\(\gamma_{\text{PS-PLA}} = 5.4 \text{ mN/m}\)) has been taken from the literature.\textsuperscript{19}

Figure 5.11 shows the SEM cross-section images for both un-modified and modified PS_{b}\text{PS}\text{-}r-PMMA with the homopolymer blend on top. Table 5.5 depicts the contact angle values, as well as the corresponding interface energies. These values suggest that the surface becomes more PLA attractive when it is chemically modified by oxygen plasma and thus, they corroborate the good chemical contrast observed on the guiding patterns.
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![Figure 5.11. SEM images of PS/PLA polymer blend droplets on top of (a) un-modified and (b) modified PS$_{omega}$-r-PMMA brush](image)

### Table 5.5. Contact angle and interface energy values for PS/PLA blends on PS$_{omega}$-r-PMMA brush

<table>
<thead>
<tr>
<th>Surface</th>
<th>$\gamma_{PS-PLA}$</th>
<th>$\gamma_{PS Brush - PLA Brush}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Un-modified PS$_{omega}$-r-PMMA</td>
<td>51.4°</td>
<td>3.37 mN/m</td>
</tr>
<tr>
<td>Modified PS$_{omega}$-r-PMMA</td>
<td>147.9°</td>
<td>-4.57 mN/m</td>
</tr>
</tbody>
</table>

5.3. PLA-$b$-PDMS-$b$-PLA systems

5.3.1. PLA-$b$-PDMS-$b$-PLA synthesis

PLA-$b$-PDMS-$b$-PLA is based on the design of BCPs containing siloxane units with a very strong segregation between components ($\chi = 1.4$ at 298K)\(^1\). This BCP has been synthezized by LCPO and Arkema, and the targeted structures are the same as for PS-$b$-PLA. Figure 5.12 describes the synthetic pathway used to synthetize PLA-$b$-PDMS-$b$-PLA. Low molecular weight $\alpha,\omega$-bi-functionalized PDMS with hydroxyl groups were used as macoinitiators for the controlled growth of PLA blocks. This synthesis was performed using triflic acid as catalyst for the reaction to obtain well defined ABA triblock copolymers. On the other hand, the macromolecular specifications of the lamellar BCP are summarized in Table 5.6.

![Figure 5.12. Synthetic pathway used for the synthesis of PLA-$b$-PDMS-$b$-PLA](image)
Table 5.6. Macromolecular specifications of PLA-b-PDMS-b-PLA BCP. Macroinitiator M₀ was determined by SEC using PS standards, BCP M₀ and volume fraction by ¹H-NMR, PDI by SEC in THF and the morphology by SAXS.

<table>
<thead>
<tr>
<th>M₀, Macroin.</th>
<th>M₀, BCP</th>
<th>PDI</th>
<th>Volume fraction (Macroin. / PLA)</th>
<th>Morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 kg/mol</td>
<td>12.5 kg/mol</td>
<td>1.2</td>
<td>0.47/0.52</td>
<td>Lamellae</td>
</tr>
</tbody>
</table>

5.3.2. PLA-b-PDMS-b-PLA self-assembly

In order to guide PLA-b-PDMS-b-PLA on chemical guiding patterns, a neutral surface has to be found as it has been done for PS-b-PLA. The process is challenging due to the fact that PDMS tends to dewet, leading to a non-uniform layer on the substrate.

PLA-b-PDMS-b-PLA solutions were prepared in a butyl acetate (BA) solution since it shows neutral selectivity to PLA and PDMS. Table 5.7 depicts the calculated relative energy differences for PLA and PDMS in BA compared with toluene and PGMEA. The average solubility parameters for PDMS are δᵣ = 14.6, δᵣ = 4.9 and δᵣ = 0.9³⁰.

Table 5.7. Relative energy difference calculated for toluene, PGMEA and BA with respect to PLA and PDMS. PLA and PDMS radius are 10.7 and 8.9, respectively ¹⁷, ²¹.

<table>
<thead>
<tr>
<th>Compound</th>
<th>RED₀,₀LA</th>
<th>RED₀,₀DMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>0.849</td>
<td>0.886</td>
</tr>
<tr>
<td>PGMEA</td>
<td>0.621</td>
<td>1.126</td>
</tr>
<tr>
<td>Butyl acetate</td>
<td>0.629</td>
<td>0.769</td>
</tr>
</tbody>
</table>

As for PS-b-PLA, four different brush layer materials based on PS-ᵣ-PMMA chemistry have been investigated (Table 5.2) by varying the BCP film thickness and annealing conditions. Figure 5.13 shows the self-assembly behavior of PLA-b-PDMS-b-PLA on different PS-ᵣ-PMMA brush materials. The film thickness used is the same for all samples (34 nm) and the BCP has been annealed at 100°C for 24h under vacuum which were the optimal conditions found for PS-b-PLA.

As it can be observed from the SEM images, a parallel oriented morphology is observed when PSᵣᵣ-ᵣ-PMMA is used as a brush layer due to the fact that there is a very strong affinity between the substrate and one of the domains. For brush layers of 60% and 70% of PS content, some perpendicular lamellae are observed on the surface, but it is not enough to create a total or almost neutral flavor necessary for chemical epitaxy processes. On the other hand, the BCP self-assembly behavior has been also tested directly on 20 nm silicon dioxide layer on silicon, getting some parallel and perpendicular oriented lamellae areas.
The BCP self-assembly behavior has shown more perpendicular oriented lamellae regions when PS<sub>60</sub>-r-PMMMA had been used. Therefore, in order to further explore the wetting behavior, a study as a function of BCP film thickness has been performed.

From SEM results shown in Figure 5.14, it is observed that the BCP morphology is, as for PS-b-PLA, very sensitive to its film thickness. Nevertheless, despite having studied a broad range of film thicknesses, a large area with perpendicular morphology has not been found. That is, that no neutral layer which enables the balance of surface free energies has been found for this BCP.

Since no neutral layer has been found, and in order to change the brush wetting properties, another approach has been tested. PDMS-OH brush (see polymer specifications depicted in Table 5.8) has been spin-coated on PS<sub>60</sub>-r-PMMMA which is the brush that has shown a larger area with fingerprint morphology, and annealed under the same conditions as PS<sub>60</sub>-r-PMMMA was (230°C for 5 min in a N<sub>2</sub> flow). Then the BCP has been spin-coated at 2000 rpm on the top of the brush from a 1.5% solution in BA and annealed at 100°C for 24 h in a vacuum oven.
Table 5.8. PDMS-OH brush layer specifications

<table>
<thead>
<tr>
<th>Brush material</th>
<th>$M_n$</th>
<th>PDI</th>
<th>PDMS Volume fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS-OH</td>
<td>3 kg/mol</td>
<td>2.23</td>
<td>1</td>
</tr>
</tbody>
</table>

Figure 5.15 shows a SEM image of a large area in which the BCP has been oriented perpendicularly to the substrate when PDMS-OH brush has been spin-coated on 8.6 nm of PS$_{1000}$-r-PMMA. Therefore, it can be concluded that it has been found a neutral layer to guide the BCP by using a bi-layer brush approach.

![Figure 5.15. SEM image of lamellar PLA-b-PDMS-b-PLA self-assembly for a film thickness of 34 nm annealed at 100°C for 24 h under vacuum on top of PDMS-OH / PS$_{1000}$-r-PMMA bi-layer brush](image)

5.3.3. PLA-b-PDMS-b-PLA directed self-assembly by chemical epitaxy

The alignment of PLA-b-PDMS-b-PLA has been investigated on chemical guiding patterns using PS$_{1000}$-r-PMMA brush layer and soft oxygen plasma conditions, although a proper neutral surface has been not found. The BCP has been spin-coated and processed with the optimal conditions found in free-surface (2000 rpm and 100°C for 24h under vacuum). Figure 5.16 shows a SEM image of a DSA pattern. Some degree of dewetting along with some degree of alignment can be observed. This means that, as it has been previously discussed, there exists some chemical contrast on the surface to guide the BCP but not enough to induce the BCP perpendicular morphology in the whole sample, since the surface is not neutral.

![Figure 5.16. SEM images of PLA-b-PDMS-b-PLA DSA for $L_n = L_o$ and 100 nm pitch](image)
5.3.4. PLA-\(b\)-PDMS-\(b\)-PLA directed self-assembly by chemo/grapho epitaxy

As the DSA process based on chemical epitaxy did not work to align PS-\(b\)-PDMS-\(b\)-PLA, a graphoepitaxy approach has been implemented in order to study the alignment of the BCP when it is confined. This process, represented in Figure 5.17, is the same as the one described in chapter 4. It consists of 6-steps: (i) e-beam writing on PMMA resist, (ii) PMMA development, (iii) silicon etching, (iv) resist removal, (v) polymer brush grafting on silicon, and (vi) BCP spin-coating.

![Figure 5.17. Schematic representation of the graphoepitaxy process for PLA-\(b\)-PDMS-\(b\)-PLA by means of e-beam lithography](image)

For this BCP, the PS\(_{60}\)-PMMA brush layer has been used, since it is the one which has shown more neutral affinity with the BCP. After the creation of the topographical guiding patterns, the brush is spin-coated from a 2\% PGMEA solution at 5000 rpm in order to graft only the bottom of the trenches. By this way, the bottom will be a neutral surface for both domains, and the silicon walls will be more attractive to PDMS blocks.

Then, the non-grafted brush is removed and a 1.5\% BA PLA-\(b\)-PDMS-\(b\)-PLA solution is spin-coated at 2500 rpm and annealed at 100°C for 24h in vacuum. Figure 5.18 shows a schematic representation of a silicon trench, in which the brush has been only grafted at the bottom, thus presenting a strong PDMS affinity at the walls. PLA-\(b\)-PDMS-\(b\)-PLA DSA by graphoepitaxy results are shown in Figure 5.19 for two different trench widths. As seen from top-view SEM images, a good degree of alignment is achieved, even for trench width of 6\(L_0\).

![Figure 5.18. Schematic representation of the graphoepitaxy process for PLA-\(b\)-PDMS-\(b\)-PLA](image)
Figure 5.19. SEM images of PLA-b-PDMS-b-PLA DSA by graphoepitaxy for a guiding pattern of (a) 200 nm pitch and 50 nm trench width and (b) 300 nm pitch and 150 nm trench width, annealed at 100°C for 24h.

As previously discussed for PS-b-PLA, the annealing times used for BCP were too long for application in industry. Therefore, a wide range of annealing temperatures (100°C to 180°C) and times (10 min to 30 min) have been tested in order to know if there were more suitable conditions with the same alignment results.

Figure 5.20 shows a SEM image with the PLA-b-PDMS-b-PLA DSA results which present optimal alignment conditions at higher temperatures and lower times. It has been found that by increasing 50°C the annealing temperatures, the time can be reduced to 15 min, which means that the process has potential industrial application.

During the annealing tests, it has been observed that the polymer degrades at temperatures above 150°C. On the other hand, the BCP self-assembly presents a high density of defects when working at 150°C with annealing times below 15 min.

Figure 5.20. SEM images of PLA-b-PDMS-b-PLA DSA by graphoepitaxy for a guiding pattern of 200 nm pitch and 50 nm trench, annealed at 150°C for 15 min.

Nevertheless, despite having shown a good DSA when graphoepitaxy approach is used, there has been observed that the DSA pattern presents some areas in which the BCP shows a parallel orientation due to non-neutrality of the surface (see Figure 5.21).
Figure 5.21. SEM images of PLA-b-PDMS-b-PLA DSA by graphoepitaxy for a guiding pattern of 200 nm pitch and 50 nm trench, annealed at (a) 100°C for 24h and (b) 150°C for 15 min, showing some parallel oriented regions.

Therefore, the surface wetting behavior has been further investigated, and in order to slightly change the affinity of the brush at the bottom of the trench an alternative step has been introduced in the overall graphoepitaxy process depicted in Figure 5.17. As observed in the new representation of the process in Figure 5.22, this new step consists in changing the brush affinity before BCP spin-coating, by exposing the sample to a brief dose of oxygen plasma (10 sccm O₂, 150W for 5 s). When doing so, the brush surface is slightly oxidized and therefore there is a change in its chemical affinity.

Figure 5.22. Chemo/grapho epitaxy overall process for PLA-b-PDMS-b-PLA

To directly study the industrial applicability of this process, the experiments have been performed on silicon graphoepitaxy guiding patterns, and then on guiding patterns created at CEA-Leti by using DUV lithography on 30 nm SiARC substrates (see Figure 5.23). Then, the brush grafting, functionalization and BCP spin-coating steps have been performed at IMB-CNMI.

Figure 5.23. Schematics of graphoepitaxy guiding patterns created at CEA-Leti
SEM images of the chemo/grapho epitaxy DSA process are shown in Figure 5.24 for different guiding pattern dimensions resulting in density multiplication factors up to 16L₀. It can be observed that the BCP shows a good alignment when using this new approach, with very low defectivity. Moreover, it is observed that, in contrast with conventional graphoepitaxy approach, all the patterned area shows a perpendicular morphology, demonstrating thus that the surface is more suitable for the DSA process.

On the other hand, it is seen that the BCP pitch is different depending on the guiding pattern dimensions. As it has been experimentally and theoretically corroborated, BCP tends to adjust its morphology depending on the separation between trenches. Table 5.9 shows the pitch the BCP adapts as a function of the guiding pattern dimensions. As observed, BCP pitch down to 20.9 nm can be obtained.

![Figure 5.24. SEM images of PLA-b-PDMS-b-PLA DSA by chemo/grapho epitaxy for guiding pattern trench widths of 230 nm and (a) 135 nm, (b) 235 nm and (c) 335 nm pitch, and annealed at 150°C for 15 min](image)

<table>
<thead>
<tr>
<th>Guiding width</th>
<th>Trench width</th>
<th>Density mult. factor</th>
<th>BCP pitch</th>
</tr>
</thead>
<tbody>
<tr>
<td>365 nm</td>
<td>230 nm</td>
<td>6L₀</td>
<td>22.5 nm</td>
</tr>
<tr>
<td>465 nm</td>
<td>230 nm</td>
<td>11L₀</td>
<td>21.4 nm</td>
</tr>
<tr>
<td>565 nm</td>
<td>230 nm</td>
<td>16L₀</td>
<td>20.9 nm</td>
</tr>
</tbody>
</table>

In order to study how the BCP behaves at the bottom of the guiding pattern, SEM cross-section characterization has been performed. Despite not having enough resolution, from Figure 5.25, it can be observed that the BCP domains present the perpendicular orientation through the whole film down to the bottom of the guiding pattern. This indicates that there is no wetting layer at the bottom, demonstrating thus the neutrality of the brush for the two BCP domains.
In order to evaluate the BCP film thickness behavior on the final DSA pattern, two different BCP fillings have been tried. Figure 5.26 shows SEM images, and a schematic representation of three different BCP fillings. As observed from the images, in the three situations there is some BCP alignment, although when the pattern is overfilled (Figure 5.26.c) there are some regions in which the BCP is oriented parallel to the substrate.

To determine the BCP filling of the two first samples, they have been characterized by AFM. As observed in Figure 5.27, for the first situation (Figure 5.26.a), there is not enough contrast on the topography image due to the small BCP filling (15 nm). However, when the BCP fills the 30 nm SiARC guiding patterns, there is enough contrast in both topography and phase AFM images.

On the other hand, the high contrast of the phase AFM images reveal that there is no PDMS wetting layer on the top of the guiding patterns, thus allowing the pattern transfer into the substrate.
The results presented for PLA-b-PDMS-b-PLA are very promising for various reasons. First, there has been found a way to get the same BCP orientation on the whole guiding pattern with very high density multiplication factors and with very low defectivity. On the other hand, both the substrates and the processing conditions used, demonstrate that the process is feasible for industrial integration.
5.4. Summary and conclusions

Two different high-$\chi$ BCP systems have been designed by macromolecular engineering in order to produce sub-10 nm lithographic structures for line/space patterning. These two BCP systems have been chosen since their segregation strength was expected to be higher than the one corresponding to PS-$b$-PMMA system. This has been confirmed by the study of their self-assembly behavior in thin film configuration. Moreover, for both of them, their self-assembling capabilities have been investigated in order to implement several DSA processes and achieve aligned patterns.

With respect to PS-$b$-PLA, a proper brush layer which balances the interactions between the surface and both BCP domains has been found, thus leading to the perpendicular BCP orientation. Despite working with annealing temperatures very close to the PS glass transition temperature, successful results have been found, which demonstrate that it is possible to reduce the thermal annealing times enabling the process to be suitable for an industrial application. On the other hand, the formation of aligned lines by means of chemical epitaxy has been partially achieved since a chemical guiding pattern contrast has been found, but not strong enough to guide the BCP domains parallel to the guiding stripes.

For PLA-$b$-PDMS-$b$-PLA system, a novel approach has been designed, based on the combination of both chemical and graphoepitaxy methods which has provided large guided areas with density multiplication factors up to 16L0. Furthermore, this BCP has shown very remarkable DSA results with respect to integration capability. Indeed, the integration of this system has shown its ability to define sub-20 nm structures with processing conditions compatible with the industry requirements.
5.5. References


15. Hansen, C. M. *The three dimensional solubility parameter and solvent diffusion coefficient.* (1967).


