Determination of the interfacial energies in chemical guiding patterns for directed self-assembly of block co-polymers

Laura Evangelio\textsuperscript{1,2}, Matteo Lorenzoni\textsuperscript{3}, Jordi Fraxedas\textsuperscript{2}, Francesc Pérez-Murano\textsuperscript{1},

\textsuperscript{1}Institut de Microelectrònica de Barcelona (IMB-CNM, CSIC)
\textsuperscript{2}Institut Català de Nanociència i Nanotecnologia (ICN2, CSIC)
Campus UAB, 08193-Bellaterra, Barcelona

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\Rightarrow \text{The morphology of the BCP depends on the ratio between the molecular weights of both blocks:}
The block copolymer pitch ($L_0$) depends on its molecular weight.

Polymer chain length = Polymer period

Introduction to the Directed Self-Assembly (DSA) of Block Copolymers (BCP)

Intrinsic property of BCP to self-assemble

Traditional lithographic techniques

Guiding of the BCP

Chemical epitaxy

Graphoepitaxy
**DIRECTED SELF-ASSEMBLY METHODS**

**Graphoepitaxy**

Lithography resist

Si

→

Si

**Chemical epitaxy**

Almost neutral area

Preferential area for one of the blocks

Si

→

Si

**CHEMICAL EPITAXY METHODS**

**LINE Process (Wisconsin)**


**IBM Process**


**SMART Process**

PROCESS AND MATERIALS

1. Brush (grafting) to the silicon substrate
2. Electron beam lithography
3. O₂ plasma functionalization

4. DSA of PS-b-PMMA

→ **BCP:** PS-b-PMMA
  
  \[(hp = \frac{L_0}{2} = 18.5 \text{ nm}, 14 \text{ nm}, 11 \text{ nm})\]
  
  and thermal annealing

→ **Brush layer:** PS-OH, PS-r-PMMA using several annealing conditions

→ **Chemical functionalization:** Exposure to O₂ plasma (two conditions: soft, strong)

DENSITY MULTIPLICATION AND CHEMICAL EPITAXY

**SIA Lithography Roadmap 2013**

**Figure LITH4A  DSA Techniques for Lines and Spaces**
ROLE OF INTERFACE ENERGIES IN THE CHEMICAL EPITAXY PROCESS

The proper achievement of high density multiplication factors requires considering multiple parameters simultaneously.

### Dimensional Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_s$</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 lamella period</td>
</tr>
<tr>
<td>$d$</td>
<td>Film thickness</td>
</tr>
</tbody>
</table>

### Material Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi N$</td>
<td>Flory Huggins parameter · degree of polymerization</td>
</tr>
<tr>
<td>$R_{eo}$</td>
<td>Mean square distance of BCP chains</td>
</tr>
<tr>
<td>$\kappa N$</td>
<td>Inverse isothermal compressibility · 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 segment species with the confining boundaries</td>
</tr>
</tbody>
</table>

Δ$\gamma = \gamma_{SA} - \gamma_{SB}$ is the main driving force in directed self-assembly by chemical epitaxy.

EXPERIMENTAL DETERMINATION OF INTERFACE ENERGIES

Δ$\gamma$ is determined from the Young equation by de-wetting experiments:

$$\Delta \gamma = \gamma_{SA} - \gamma_{SB} = \gamma_{AB} \cdot \cos (\phi_{AB})$$


实验过程

1. 刷 (grafting) 到硅基板
2. PS/PMMA 混合溶液 spin-coating
3. PS-PMMA dewetting

$\phi_{AB}$: 液面张力

取自文献

$\cos (\phi_{AB})$ 是通过实验确定的

$\phi_{AB} < 90^\circ$: 更多亲和力到块 B
$\phi_{AB} = 90^\circ$: 中性表面
$\phi_{AB} > 90^\circ$: 更多亲和力到块 A
Homopolymer blends dewetting on polymer brush surfaces

SEM characterization

AFM characterization

Topography
Young Modulus
Adhesion
Deformation

Un-modified PS-Oh brush
Modified PS-OH brush

Δγ = γ\text{SA} - γ\text{SB} = γ_{AB} \cdot \cos(\phi_{AB})


<table>
<thead>
<tr>
<th>Processing conditions</th>
<th>Background stripe</th>
<th>Guiding stripe (soft plasma)</th>
<th>Guiding stripe (hard-plasma)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Brush material</strong></td>
<td><strong>BCP Annealing</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS-OH</td>
<td>230°C for 10 min in N₂</td>
<td>0.35</td>
<td>-0.38</td>
</tr>
<tr>
<td>PS-OH</td>
<td>200°C for 20 min in Hot-Plate</td>
<td>0.40</td>
<td>-0.80</td>
</tr>
<tr>
<td>PS_{0.69-γ}-PMMA_{0.31}</td>
<td>230°C for 10 min in N₂</td>
<td>0.13</td>
<td>-0.50</td>
</tr>
</tbody>
</table>

The sets of interface energies are the ones that provide suitable conditions for high multiplication factors.

**Experimental determination of interface energies**


**Density multiplication and interface energies**

Optimal conditions for PS-b-PMMA of several pitch dimensions

(Narrow stripes) \( \eta = 2 \)

(Wide stripes) \( \eta = 6 \)

(Wide stripes) \( \eta = 5 \)

Δγ [mN/m]

<table>
<thead>
<tr>
<th>Background</th>
<th>Guiding stripe</th>
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<tbody>
<tr>
<td>1.5 Lo</td>
<td>0.5 Lo</td>
</tr>
<tr>
<td>3.5 Lo</td>
<td>2.5 Lo</td>
</tr>
<tr>
<td>2.5 Lo</td>
<td>2.5 Lo</td>
</tr>
</tbody>
</table>
HIGH DENSITY MULTIPLICATION FACTORS WITH PS-b-PMMA 11 nm hp

η=3  η=4  η=5

Δγ [mN/m]  0.13  -0.50

PS-PMMA 11 nm hp

INFLUENCE OF OXYGEN PLASMA FUNCTIONALIZATION STRENGTH

Soft plasma  Hard plasma

Δγ  0.40  -0.80

Δγ  0.40  -0.91

PS-PMMA 14 nm hp
INFLUENCE OF OXYGEN PLASMA FUNCTIONALIZATION STRENGTH

**PS-PMMA 11 nm hp**

Soft plasma

Hard plasma

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<tr>
<th></th>
<th>Background</th>
<th>Guiding stripe</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Δγ</strong></td>
<td>0.13</td>
<td>-0.56</td>
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NEW METHODS FOR CHEMICAL GUIDING PATTERNS

1. **AFM based nanolithography**

2. **Electron beam nanolithography direct writing**


SUMMARY

• Density multiplication by wide guiding stripes can be achieved by properly tuning of the interface energies
• Strength of interface energies can be quantified from dewetting experiments

• Density multiplication factor of $x6$ has been achieved with PS-b-PMMA of 14 nm hp

• Simulations allow to predict the final DSA pattern, and suggest that the value of interface energy is lowered by the presence of residual solvent during the annealing

THANK YOU FOR YOUR ATTENTION

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