Development of block copolymer systems for directed self assembly at the University of Queensland

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Australian Institute for Bioengineering and Nanotechnology

• 16,000 m² research facility.
• 450 researchers with backgrounds ranging from chemistry to engineering and biology.
• State of the art laboratories and facilities for polymer synthesis, characterisation, nanofabrication and metrology.
Lithography research at AIBN/UQ

- 2003-2004: 157 nm pellicles (Sematech)
- 2005-2007: High index resist polymers (Sematech)
- 2007-2010: Chain scissioning resists (Non-CAR) for 193 nm immersion and EUVL (Intel and Sematech)
- 2008-present: Directed self assembly (Intel and now Dow)
Current research motivations

• Can we design new materials to overcome the triangle of death to simultaneously improve RLS?

Cho et al., EUVL & Litho extensions, 2009.
• Can we design new materials to overcome the triangle of death to simultaneously improve RLS?
Our approaches

1. Healing of roughness

2. Achieving sub-10 nm resolution

Concept 2 – DSA of block copolymers

Imelda Keen
Han Hao (Elliot) Cheng
Anguang Yu
Block copolymers (BCPs) self assemble into different morphologies

- Dependent on:
  - Volume fraction \( (f_A) \)
  - Flory-Huggins interaction parameter \( (\chi_{AB}) \)

- Useful for:
  - Batteries
  - Membranes
  - Nanofabrication

Adapted from Materials Today, 2010, 13, 42
Graphoepitaxy

- Uses topographical structures to guide assembly
Capabilities and limitations

- Pattern multiplication
- Sub-lithographic resolution
- PS-\(b\)-PMMA widely studied
  - Low \(\chi\) parameter
  - Most processes require treatments to ‘freeze’ the template
  - Poor etch selectivity

*Cheng et al ACS Nano, 2010, 4 (8), pp 4815–4823*
A high $\chi$ system

$$\begin{align*}
\text{Br} & \text{O} - \text{CH}_2 - \text{CH} - \text{OH} \\
\text{Br} & \text{O} - \text{CH}_2 - \text{CH} - \text{OH}
\end{align*}$$

ATRP ROP

$$\begin{align*}
\text{Br} & \text{O} - \text{CH}_2 - \text{CH} - \text{OH} \\
\text{Br} & \text{O} - \text{CH}_2 - \text{CH} - \text{OH}
\end{align*}$$

GPC

Well defined polymers

<table>
<thead>
<tr>
<th>$M_W$  (kDa)</th>
<th>vol % PDLA</th>
<th>$D_M$</th>
<th>Bulk $L_0$ - SAXS (nm)</th>
<th>Bulk domain size - SAXS (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.0</td>
<td>50</td>
<td>1.25</td>
<td>15.9</td>
<td>8.0</td>
</tr>
<tr>
<td>14.7</td>
<td>48</td>
<td>1.14</td>
<td>16.5</td>
<td>8.3</td>
</tr>
<tr>
<td>16.5</td>
<td>46</td>
<td>1.18</td>
<td>19.8</td>
<td>9.9</td>
</tr>
<tr>
<td>21.0</td>
<td>48</td>
<td>1.25</td>
<td>21.3</td>
<td>10.7</td>
</tr>
</tbody>
</table>

_GPC_, 2012, 28 (45), pp 15876–15888

_Langmuir_, 2012, 28 (45), pp 15876–15888
Interactions of blocks with a surface matter for thin films

Surface interactions favour red block

Surface interactions are neutral

Surface interactions favour grey block
Crosslinkable polymers for surface energy modification

0-99% 0-99% 1%

Styrene + MMA + latent crosslinker

Surface energy tuning

- Series of random copolymers synthesised

- Spin coated on wafers and UV crosslinked

Surface energy of substrates could be tuned

Surface Energy (dyn/cm)

%PS in film
Neutral surfaces identified

Neutral window observed between 32 and 38% PS

Annealing temperature – 100 °C

Inset to SEM shows GISAXS

Langmuir, 2012, 28 (45), pp 15876–15888
Directed self assembly - graphoepitaxy

**Litho**
- DSA with PS-\textit{b}-PLA
  - Resist freezing not required
  - Can be spin coated from a non-solvent for PHOST based resists
  - $T_{\text{Anneal}} \sim 100 \, ^\circ\text{C}$ (< most resists)
  - Etch selectivity for PS to PLA is 1:4

**DSA**

**Etch**

Keen, ... Blakey \textit{et al.}, \textit{manuscript in preparation} 2013.
Uniformity of coverage (2 $L_0$)

BCP coverage for 48.3 nm CD lines 21 k PS-$b$-PDLA

CD Shrink: 48 - 12 nm (75%)
Excellent BCP coverage

30% reduction in LER observed
Domain Stretching

- # of $L_0$ are quantized such that domains stretch/compress to be commensurate with the trenches in which they are confined.
- Consistent with literature on confined cylindrical domains

Keen, ... Blakey et al., manuscript in preparation 2013.
Defectivity increases for higher degrees of stretching and larger confinement volumes.
Higher $\chi$ Systems?

- PS-$b$-PMMA limited to pitch of $\sim20$ nm
- PS-$b$-PLA limited to pitch of $\sim16$ nm
- There are a number of promising high $\chi$ systems e.g. PS-$b$-PHOST (1.37), PS-$b$-PAA (1.5) and PS-$b$-P4VP (0.3)
- This requires synthesis of new polymer systems and optimization of processing etc.
Effect of additives

- Doping additives to PS-b-PMMA
  - Can we increase the $\chi$ parameter of BCPs?
  - Can we tune $L_0$ / commensurability?
  - Can we tune morphology?

- Potential advantages include:
  - Use currently available BCPs
    - Shallow learning curve?
    - Less need for more polymer synthesis
    - Reduced defectivity?
Can additives be used to influence $\chi$?

Addition of additives (5 volume %) induced order in a disordered PS-b-PMMA (10k-b-10k).

- $\chi$ has effectively been increased!
- Effect observed as low as 5k-b-5k $\Rightarrow \chi$ at least tripled
Morphology of BCPs can also be tuned

20% additive

30% additive

Gyroid

Hexagonal

50% additive

Cubic BCC
Works for Thin Films - $L_0$ Tuning

**No additive**

$L_0 = 36.2$ nm  

**25% additive**

$L_0 = 40.7$ nm

Same neutral surface was used in both cases

Will tuning of $L_0$ result in less defects?
Tuning morphology in thin films

No additive

25% additive

Cylindrical/hexagonal

Lamellar

Will be discussed in more detail at SPIE
Summary

• PS-b-PLA
  – Demonstrated DSA of PS-PLA a high $\chi$ BCP.
  – Neutral underlay not required for narrow trenches.
  – Stretching and compression results in more defects.

• Additives
  – Additives used to increase $\chi$ of PS-b-PMMA.
  – Allows tuning of $L_0$ and morphology in bulk and thin films.
  – Potentially extends scope of PS-b-PMMA for DSA
Acknowledgements

- **PS-PLA and LER healing**
  - Ms Ya-Mi Chuang (concept 1)
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  - Dr Imelda Keen (concept 2)
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  - Dr Kevin Jack (CMM)
  - Dr Michael Leeson (Intel)
  - Dr Todd Younkin (Intel)
  - Prof. Andrew Whittaker

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  - Dr Kristofer Thurecht
  - Dr Kevin Jack

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  - ANFF-ACT
  - ANFF-Q
  - CAI
  - AIBN

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  - Linkage Projects
  - Future Fellowship
  - Linkage Infrastructure Equipment and Facilities