Directed Self-assembly of PS-b-PMMA with Ionic Liquid Addition

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Background

PROS
✓ balanced surface energy
✓ thermal annealing availability
✓ Selective removal of PMMA

CONS
✓ relatively low $\chi$
✓ limited resolution: 10-11 nm HP

Poly(styrene-b-methyl methacrylate)

Jeong et al, Materials Today 2013, 16 (12), 468
How to balance the surface energy of two blocks to maintain perpendicular morphology?

Cochran et al., Macromolecules 2003, 36 (3), 782
Zalusky et al., JACS 2002, 124 (43), 12761
Kim et al., Nano Lett. 2014 14, 148

Jeong et al, Materials Today 2013, 16 (12), 468
Background

Solvent Vapor Annealing

Top-coat

PS-b-PMMA + Ionic Liquid = PS-b-PMMA/IL blends

✓ higher $\chi$ than pure PS-b-PMMA
✓ manageable change in surface and interfacial properties
✓ thermal annealing capability with a free surface $\rightarrow$ integration-friendly

Yoshida et al., JPST, 2013, 26 (1), 55
Outline

- Ionic liquid introduction
- Orientation control by random brush
- Can PS-b-PMMA/IL enable sub-10 nm lithography?
- Initial DSA results
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Ionic Liquid

- Salt melting below 100 °C
- Composed entirely of cations and anions
- Thermal stability
- Negligible vapor pressure @r.t
- “designer solvent”
  -- all properties can be tuned by changing component ions

Why can IL addition increase $\chi$?

- solubility of chosen IL with:
  - PS: No
  - PMMA: Yes
- IL mostly goes into PMMA domain $\rightarrow$ polarity $\uparrow$
- effectively increase system $\chi$
- Induce self-assembly of BCP

Differential scanning calorimetry (DSC)

- PS-b-PMMA
- PS-b-PMMA/IL

Heat flow

Temperature/°C
Ionic Liquid

- Solubility of chosen IL with:
  - PS: No
  - PMMA: Yes
- IL mostly goes into PMMA domain → polarity↑
- Effectively increase system $\chi$ → Induce self-assembly of BCP

Miranda et al., Macromolecules 2010, 43, 10528

Bennett et al., JM3 2014, 13, 031304-1

Bulk SAXS + Self-assembly in thin film:
Enhanced phase segregation by adding IL into di-/triblock copolymer system.
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Processing Window

$\chi$

$\gamma_{PS} \approx \gamma_{PMMA}$

**PS-ran-PMMA brush**

$+IL \quad f_{PS} \downarrow$ in brush

$\chi$

$\gamma_{PS} \neq \gamma_{PMMA/IL}$

**PS-ran-PMMA brush**

"perpendicular window" of PS-b-PMMA
PW shifts to lower $f_{PS}$ with IL addition

\[ \gamma_{PS} \approx \gamma_{PMMA} \]

PS-ran-PMMA brush

+IL $f_{PS}$↓ in brush

\[ \gamma_{PS} \neq \gamma_{PMMA/IL} \]

PS-ran-PMMA brush

IL/BCP mass ratio

PS fraction ($f_{PS}$) in random brush
IL Selection

Ionic Liquid A

L₀ increases with the amount of IL added. (L₀ ∝ χ¹/₆N²/₃)

L₀ = 24.75 nm

IL%↑

IL%↓

no IL

IL Loading Ratio

IL% ↑ increases with the amount of IL added.

L₀ = 24.75 nm

25.63 nm

26.40 nm

27.35 nm
Different types of IL have different capability of increasing the $L_0$ of BCP/IL blends.

IL Selection

Ionic Liquid A
- $L_0 = 24.75$ nm
- $25.63$ nm
- $26.40$ nm
- $27.35$ nm

Ionic Liquid B
- $L_0 = 24.59$ nm
- $25.96$ nm
- $27.26$ nm
- $28.05$ nm
### IL Selection

**Ionic Liquid A**
- L_0 = 24.75 nm
- 25.63 nm
- 26.40 nm
- 27.35 nm

**Ionic Liquid B**
- L_0 = 24.59 nm
- 25.96 nm
- 27.26 nm
- 28.05 nm

**Lower IL% to achieve the same \( \chi_{\text{eff}} \) is preferred**

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**PS-b-PMMA/IL blends: a high-\( \chi \) drop-in replacement of PS-b-PMMA**
Outline

- Ionic liquid introduction
- Orientation control by random brush
- Can PS-b-PMMA/IL enable sub-10 nm lithography?
- Initial DSA results
Sub-10 nm lithography

The answer is “YES”!

By adding a small amount of IL into PS-b-PMMA, lamellas of ~19.3 nm $L_0$ is achieved via thermal annealing.
Outline

- Ionic liquid introduction
- Processing window study of PS-b-PMMA/IL blends
- Can PS-b-PMMA/IL enable sub-10 nm lithography?
- Initial DSA results
4X DSA of PS-b-PMMA/IL blends system with ~19.3nm $L_0$ is tried via LINE flow

All work performed in 300 mm FAB at IMEC
All materials from TOK, Japan
4X DSA of PS-b-PMMA/IL blends is achieved with a relatively wide processing window of line width.

After trim

BCP assembly

W=22.3 nm (1.16L₀)  W=17.4 nm (0.91L₀)  W=12.2 nm (0.63L₀)

Focus

L₀=19.3 nm

4X DSA on 78nm

Lₕ=78 nm (4.04L₀)
4X DSA of PS-b-PMMA/IL blends is achieved with a relatively wide processing window of line width.

\[
W = 33.5 \text{ nm (1.74} L_0) \approx W = 25.4 \text{ nm (1.32} L_0) \]

etched through

Detcheverry et al., Macromolecules 2010, 43, 3446

\[ L_s = 78 \text{ nm (4.04} L_0) \]
Successful 4X DSA on $L_S = 76\text{--}79 \text{ nm (within } L_0 \pm 10\% \text{ range)}$

-- similar process window: $W/L_0 = <0.6 \sim 1.2$

-- $L_S \leq 76 \text{ nm}$ is limited by 193i-litho

-- $L_S \geq 80 \text{ nm}$: wave-like alignment ("herringbone pattern")

Kim et al., Nature 2003, 424, 411
We investigate a high-$\chi$ system by blending IL into PS-b-PMMA

The change in surface/interfacial properties is manageable by tuning $f_{PS}$ in random brush layer

Successful sub-10nm DSA from lab to fab
Outlook

✓ More fundamental understanding:
  - what is the IL distribution like?
  - how does IL affect the interfacial width? ...

✓ Roughness comparison by assembling PS-b-PMMA with and without IL addition

✓ How far can we scale down in sub-10 nm lithography?
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