Design of Block Copolymers for Perpendicular Orientation of Lamellar Structures with sub-10 nm Features

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Perpendicular oriented lamellar structures by thermal annealing in a few minutes

- Fluorine- & Silicon-containing Polymethacrylates: Poly(POSS methacrylate)-b-Poly(trifluoroethyl methacrylate)
  
  **PMAPOSS-b-PTFEMA**
  

- Polysiloxane-based BCPs: Polystyrene-b-Poly(methyl vinyl siloxane)s with modified side chains
  
  **PS-b-PMVS modified BCP**
  
  T. Hayakawa et al., paper in revision
Targeting for Sub-10 nm Features

Pattern dimension $L_0 \sim a \cdot N^{2/3} \cdot \chi^{1/6}$
($N \cdot \chi > 10.5$ for micro phase separation)

$L_0$: pattern dimension
$a$: characteristic segment length
$N$: degree of polymerization
$\chi$: Flory-Huggins interaction parameter

Increasing $\chi$ can lead formation of small domains with low molecular weight BCPs.

Macromolecules 29 1091 (1996)
High-\(\chi\) BCPs for DSA

Ex. Silicon-containing BCPs

Ross at al., Nano Lett., 2007

Hillmyer at al., ACS Nano., 2010

Gopalan & Hayakawa at al., Macromolecules, 2008

Willson at al., Science, 2012

Ellison at al., Macromolecules, 2012

Control Interfaces for Orientation
Surface (Air, controlled atmospheres)

Underlayer (Substrates)

Process-friendly approaches are one of the promising technologies.

Molecular Design
Perpendicular Orientation Controllable High-chi BCPs

- Simple and easy synthesis
- Precise control of molecular weight and composition
- High repulsion
- High contrast in etch resistance
- Film uniformity (no dewetting)
- Perpendicular orientation of domains
- Thermal annealing in short time
- Easy process (top-coat free, if possible)
- Compatible with existing DSA technology

It is essential to balance many requirements in the primary structure and the thin film.
Our Strategy in Molecular Design
Perpendicular Orientation Controllable High-chi BCPs

A
Polarity: medium

B
Polarity: high or low

X
Polarity: low or high

Functional group

Side chain

Not only repulsive properties between A and B, but also between B and X in the monomer structure of a block.

Compatibility of strong repulsion and surface free energy balance
Organic-Inorganic Hybrid Block Copolymer

PMMA-\(b\)-PMAPOSS

- Strong segregation between PMMA and PMAPOSS enables self-assembly in sub 10nm dimensions
- Etch resistance of POSS group against \(O_2\) RIE for robust pattern transfer

Chemoepitaxy DSA of **PMMA-b-PMAPPOSS**

ms134, PMMA$_{17}$-b-PMAPPOSS$_9$
Mn: 10,500, PDI: 1.05, PMAPOSS fraction: 0.84

**Chemical Registration**

Thermal Annealing at 150 °C, no dewetting

$d_{sub} = 29$ nm ~ $3 \times d_0$

$d_{obs} = 9.7$ nm  5.9 Tbpsi

**collaborated with**
Dr. Hiroshi Yoshida
Hitachi Research Laboratory:
Chemoepitaxy DSA of PMMA-b-PMAPOSS

- Formation of small domains
- Not achieved the perpendicular oriented lamellar structure in thin films.
- Surface segregation of PMAPOSS results in forming PMAPOSS covered structure in the films.

PMMA-b-PMAPOSS

Surface Free Energy

PMAPOSS: 28.7 mJ/m²
PMMA: 47.2 mJ/m²

Thermal Annealing at 150 °C, no dewetting
PTFEMA, instead of PMMA

- **Surface Free Energy**
  - PTFEMA: 25.1 mJ/m²
  - PMAPPOSS: 28.7 mJ/m²
  - PMMA: 47.2 mJ/m²

- **Good degradability**
- **High polarity**

Strategy for Perpendicular Lamellar Orientation

High O₂ Etch Resistance

Polarity: Medium or Low

Segregation to Surface

Polarity: High –COO–

Polarity: Low –CF₃

(PMMA : 47.2 mJ/m²)

PMAPOSS : 28.7 mJ/m²

PTFEMA : 25.1 mJ/m²

Synthesis of PMAPOSS-b-PTFEMA

1. TFEMA
2. MeOH
Bulk Morphology

7wt% CHCl₃ Dried for 24h Sample1 (Mₙ: 32,000)

SAXS profile TEM image

PMAPOSS/PTFEMA 16/84 Mₙ: 32,000 PDI: 1.06

Intensity (a.u.)

$q$ (nm⁻¹)

1 2 3

$d$-spacing: 20.7nm

×15,000

■: POSS □: PTFEMA
ULTRA Speed AFM

One image every 6-10 seconds with heat treatment (thermal annealing)
Polysiloxane-based BCPs

Polystyrene-\(b\)-Poly(dimethyl siloxane)
PS-\(b\)-PDMS
Issues in Conventional polysiloxane-based BCPs

Organic-Si containing BCPs

PS-\textit{b}-PDMS

+ High repulsion property and high etch contrast

- Difficult to obtain uniform thin films due to the low $T_g$ of PDMS in some cases

- Segregating PDMS at the film surfaces due to its low surface free energy

Ross \textit{et al}.

Solvent Annealing method

Polysiloxane-based BCP

- High resolution \( \Rightarrow \) PS-\(b\)-PDMS modification
- Perpendicular orientation \( \Rightarrow \) side chain introduction

Targets
- \( \checkmark \) Sub-10 nm periodic features
- \( \checkmark \) perpendicularly oriented features
- \( \checkmark \) Thermal annealing
- \( \checkmark \) O\(_2\)-RIE selectivity
- \( \checkmark \) Pattern transfer
Polysiloxane-based BCP

A block

B block

C block

Polysiloxane-based BCP

A block

B block

C block

Polysiloxane-based BCP

A block

B block

C block

Polysiloxane-based BCP

A block

B block

C block

Polysiloxane-based BCP

A block

B block

C block

Polysiloxane-based BCP

A block

B block

C block

Polysiloxane-based BCP

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Polysiloxane-based BCP

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Polysiloxane-based BCP

A block

B block

C block

Polysiloxane-based BCP

A block

B block

C block

Polysiloxane-based BCP

A block

B block

C block

Polysiloxane-based BCP

A block

B block

C block

Polysiloxane-based BCP
Microphase-separated Structures in Thin Films

Fingerprint pattern was observed on as cast film.
Optimum thermal annealing promotes microphase separation.
17 nm periodic line pattern was observed. Both high resolution and perpendicular orientation were achieved with new BCP.
New designed high-chi BCPs gave perpendicular oriented lamellar structures in thin films by atmospheric thermal annealing at 130 °C for 1-3 min.

Both high resolution and perpendicular orientation were achieved with new BCPs.
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