New Photoresists and Processing Methods for scCO$_2$ Development

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Outline

• Background on scCO$_2$ processing
  – Equipment for dissolution studies

Overview

• Positive-tone resist development
  – Silylation
    – *Intrinsic positive-tone*

• Cosolvent addition for enhanced solubility of novel resist materials
  – scCO$_2$ development of EUV resist
  – HFCVD patterning and processing (MIT collaboration)

• *Non-fluorinated scCO$_2$ developable resist*
Advantages of scCO\textsubscript{2} and Industrial Applications

- Photoresist and etch residue removal
  - Post metal etch
  - Post oxide etch
- Post-ash cleaning
- FEOL residue removal
- K-value restoration
- MEMs non-stiction drying
- Post CMP cleaning

**Desirable Properties**
- Liquid-like and variable density
- Gas-like diffusivity & viscosity
  - Penetrates crevices
  - High rate of development
- Strong quadrupole moment
  - Dissolves fluorinated polymers (193nm, 157nm)
- No surface tension
  - Eliminates pattern collapse in dense, high aspect ratio features

**Environmental benefits**
- Gas collected and purified from industrial effluents and not generated
- Reduce water consumption and replace hazardous chemical developers
- Non-flammable, non-toxic, abundant, recyclable
- Modest operating condition

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**NSF/SRC ERC for Environmentally Benign Semiconductor Manufacturing**
DRM Equipment

CO₂ source

High pressure pump

Preheat coil

Pressure reading

Temperature reading

Vessel #1

Temperature reading

Pressure & temperature reading

Vessel #2

Pressure & temperature reading

Micro-metering valve

Reflected beam into detector

Laser in

Detector

Laser (632.8nm)
Measurement of Film Dissolution
Principles of Interferometry

Thickness period

\[ d_p = \frac{\lambda}{2\left[n_2^2 - n_1^2 \sin^2 \theta_1 \right]^{1/2}} \]

Assumptions:
• Non-swelling
• One optically distinct moving boundary
• Film dissolves at constant rate

scCO\(_2\) development
• Swelling is expected
• Fluid equilibration, swelling, and dissolution occur simultaneously
• Density and refractive index of solvent vary with P, T
• 7/8” thick quartz glass window

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Random Copolymer Dissolution Selectivity

High solubility in CO$_2$

- Time varying rates
- Complete development of film

Low solubility in scCO$_2$

- Very slow rate of dissolution
- Incomplete development
Dissolution Rate and Completeness for THPMA-F$_7$MA

Amplitude of oscillation

\[ R_+^o = \left( \frac{n_1 - n_3}{n_1 + n_3} \right)^2 \]
\[ R_-^o = \left( \frac{n_1 n_3 - n_2^2}{n_1 n_3 + n_2^2} \right)^2 \]

Thickness period

\[ d_p = \frac{\lambda}{2\sqrt{n_2^2 - n_1^2 \sin^2 \theta_1}}^{1/2} \]
Positive-tone scCO$_2$ Developable Resists

I. Put a non-polar group on - Silylation

II. Take a polar group off – Enthalpic, entropic manipulations
DESIRE for Positive-tone CO₂ Development

Insoluble in CO₂

Soluble in CO₂

THPMA-b-F7MA

hv

H+ Chemical Amplification

SCCO₂

HMDS

hv Flood expose

Negative tone

Positive tone

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Contrasting Feature Profiles – from Negative-tone to Positive

Profilometer Plots of Patterns

*TMDS – Tetramethyl disilazane
Depth of Silylation Reaction

- TMDS, more mobile and more polar than HMDS, offers greater vertical diffusion in more polar exposed regions
Silylated Positive-tone \text{scCO}_2\text{ Developed Resist}

Negative-tone features \textasciitilde100nm
Can we achieve positive-tone for block copolymers?

Sundararajan, Ph.D.
V. Pham
Intrinsic Positive-tone Resist for scCO$_2$

Patterning with 248nm and E-beam demonstrated

Synthesized:
Polymer A191 (x = 40, y = 60, feed ratio)
Polymer A192 (x = 60, y = 40, feed ratio)
Positive Tone scCO$_2$ Photoresist Systems

$\text{hv, } H^+$

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CO$_2$ – Cosolvent – Polymer Interactions

Peter Nguyen
Nelson Felix
Victor Pham

scCO$_2$

scCO$_2$ + PPA

scCO$_2$ + PPA + CH$_2$Cl$_2$

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Effect of Cosolvents with \(\text{scCO}_2\)

- Negative tone EUV resist
- Insoluble in pure supercritical \(\text{CO}_2\)
- Soluble in \(\text{scCO}_2\) when cosolvents are added to supercritical fluid.

Poly(chloromethylstyrene-co-trimethylsilylstyrene)

\[
\begin{align*}
\text{CH}_2 & - \text{CH} & \text{CH} & - \text{CH} \\
\text{H}_3 \text{C} & - \text{Si} & - \text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_2 \text{Cl} & \text{CH}_3
\end{align*}
\]

\(m = 90, n = 10\)

- \(P = 5000\) psi, \(T = 45^\circ\text{C}\), \(t = 10\) mins

<table>
<thead>
<tr>
<th>Organic Solvent</th>
<th>Amount Added</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrahydrofuran (THF) (10 min)</td>
<td>2 vol%</td>
<td>Film removed</td>
</tr>
<tr>
<td>Tetrahydrofuran (THF) (5 min)</td>
<td>2 vol%</td>
<td>Film removed</td>
</tr>
<tr>
<td>Tetrahydrofuran (THF) (1 min)</td>
<td>2 vol%</td>
<td>Film removed</td>
</tr>
<tr>
<td>Isopropanol (IPA) (10 min)</td>
<td>6 vol%</td>
<td>Film removed</td>
</tr>
<tr>
<td>Isopropanol (IPA) (10 min)</td>
<td>2 vol%</td>
<td>Clouding of film</td>
</tr>
<tr>
<td>Ethanol (EtOH) (10 min)</td>
<td>2 vol%</td>
<td>No effect</td>
</tr>
<tr>
<td>Methanol (MeOH) (10 min)</td>
<td>2 vol%</td>
<td>No effect</td>
</tr>
</tbody>
</table>
E-beam resists deposited by CVD

- A negative-tone e-beam resist, glycidyl methacrylate (GMA), deposited by hot filament CVD at MIT (Gleason Group).
- GMA block insoluble in scCO$_2$, fluorinated repeat unit (FAA) added to form a block copolymer soluble in scCO$_2$.

Low FAA content (37%): soluble in 2% ethanol/ scCO$_2$ or 2% THF/ scCO$_2$

High FAA content (65%): scCO$_2$ soluble

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Non-fluorinated Resist for scCO$_2$

Molecular glass as resist for low LER

248 nm exposure
Developed in CO$_2$ at ~1000 psi, 40°C
Summary

- Dissolution rate measurement
- Positive-tone resist development
  - Silylation
  - Intrinsic positive-tone
- Experimental and theoretical work on cosolvent addition for development and cleaning
  - \( \text{scCO}_2 \) development of EUV resist
  - HFCVD patterning and processing
- Non-fluorinated resist systems
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