Achieving Small Dimensions with an Environmentally Friendly Solvent: Photoresist Development Using Supercritical CO$_2$

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Outline

• Supercritical CO$_2$ as a development solvent
  – Advantages
  – Use with polymeric photoresist systems

• Small molecule photoresists
  – Potential advantages
  – Solubility in scCO$_2$
  – Patterning performance
Supercritical CO₂ Basics

- **Supercritical CO₂**
  - Tunable, non-polar solvent with the ability to dissolve select non-polar materials
  - T<sub>c</sub> = 31C, P<sub>c</sub> = 1070psi (77 bar)

Supercritical CO${}_2$ in Industry

- Extraction of essential oils from organic matter
  - Cinnamon, ginger, sandalwood, etc
  - Pharmaceutical applications

- Decaffeination of coffee
  - CO${}_2$ replaced CH$_2$Cl$_2$ as solvent, removed only caffeine

- Dry Cleaning
  - Addition of surfactants

- Wafer cleaning
  - BOC Edwards DFP-200
  - Critical Point Dryer
# Next Generation Lithography: Key Problems

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<th>Pattern Collapse</th>
<th>Non-polar Materials</th>
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<td>Reduce surface tension</td>
<td>Low-κ applications</td>
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### Pattern Variations

- Non-polar Materials
  - Low-κ applications

### Pattern Collapse

- **Formula:**
  \[ P = \frac{\sigma}{R} = \frac{2\sigma \cos \theta}{d} \]

- **Condition:**
  @ 50nm L/S, aspect ratios >2:1 collapse w/ water

### Non-polar Materials

- Lack of appropriate non-polar developers
  - Must use multilplicative subtractive steps

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Advantages of Supercritical CO$_2$ Development

Elimination of organic solvents and ultra-pure water during processing

2 gram DRAM chip $\rightarrow$ 32 kg of water

Liquid-like density, Tunable Solvating Power

Gas-like transport

Penetrates crevices, no residue

Harmful solvents are cleanly separated via depressurization

No surface tension, eliminates pattern collapse

Fluorinated scCO2 Soluble Photoresists

- First platform for soluble polymeric photoresists
  - Copolymerize traditional photoresist monomers with fluorinated monomers

- Negative tone

\[
\begin{align*}
\text{Soluble} & : \quad \text{Insoluble} \\
\text{Sundararajan, et al. 193 nm exposure.}
\end{align*}
\]

- Block copolymer (Cornell) and random copolymer (UNC) versions demonstrated.


Positive Tone Resists for scCO\textsubscript{2} Development

Two-step positive-tone

\[
\begin{align*}
\text{PAG} & \quad \text{hv} \quad \text{H}^+ \\
\text{HMDS} & \quad \Delta \\
\end{align*}
\]


- Balance must be struck between resist solubility (increase F) and contrast (increase functionality)
Resist Fluorination

• Advantages
  – High transparency at 193 nm, 157 nm exposure wavelengths
    • Library of fluorinated monomers
  – Simple to increase scCO2 solubility with monomer inclusion

• Disadvantages
  – Low plasma etch resistance of F-containing structures
  – Surface compatibility: low surface energy
  – Low glass transition temperatures (Tg)
    • Difficult to keep sharp pattern shape
    • Low contrast
Reduce Fluorination

Perfluorinated octyl compounds have been shown to bioaccumulate and disrupt cellular functions.

Environmentally friendly? → reduce need for fluorination
Reducing Fluorination: Using Cosolvents

- Increase solvent density
- Tune polarity of fluid
- Specific interaction with a comonomer

- 1 vol% ethanol .... very little effect
- 2 vol% ethanol .... 100% removal

2 vol% ethanol (1.5 mol%, 1.6 wt%) in scCO₂
P = 5000 psi, T = 45°C, t = 10 min

Additives for Processing Conventional Resists

- Patent literature full of examples of surfactant libraries used for scCO2 dissolution of photoresists
  - Fluorinated or hydrocarbon tails
  - Polar or carboxylate heads
  - Mostly seen for pattern cleaning/drying

- Recent work by Micell Technologies on reactive ionic additives to impart scCO2 solubility to conventional photoresists
‘CO$_2$ Compatible Salts’

- Rather than ionic surfactants, reactive fluorinated salts added to solution
  - Interact with weak acidic groups of photoresist to impart solubility
  - Due to lower amounts of acidic groups, unexposed regions gain sufficient solubility first
  - Presence of generated acid in exposed regions inhibits reaction with photoresist

\[
\text{N}^+ (\text{CH}_2)_3 (\text{CF}_2)_5 \text{CF}_3 \\
(\text{CH}_2)_3 \\
(\text{CF}_2)_5 \\
\text{CF}_3 \\
\text{Unknown counterion}
\]

Aqueous TMAH develop

CO$_2$/CCS develop

DeYoung, J., et al., SPIE v 6153 I 2006, p 615345.
Molecular Glass Photoresists

- Small molecule size ~1-2nm
- Well defined molecular structures
  - No distribution of mass
- Low tendency towards crystallization
  - bulky irregular shape or different conformation states
- Strong intermolecular attractive forces for high Tg
  - Specific interactions such as H-bonding


Images obtained at Lawrence Berkeley National Laboratories by EUV microexposure tool
Molecular Glass Resist Solubility in scCO2

- Due to their small size, these resist materials have the potential for scCO2 solubility w/o fluorine
- Balance between size and polar functionality

Recent example

Solubility Switching

From FTIR data, solubility switch happens below <80% tBOC protection.
High Resolution MG Resist for Supercritical CO₂

Contrast Curve, 300 bar

- R = -H or -tBOC

50 nm
~3:1 aspect ratio

Dissolution Rate Measurements

\[ D = \frac{\lambda}{2\sqrt{n_2^2 - n_1^2 \sin^2(\theta)}} \]

\[ \lambda = 632.8 \text{ nm} \]

\[ n_1 = \text{solvent refractive index} \]

\[ n_2 = \text{film refractive index (\sim 1.55)} \]
Increasing pressure

40°C

Reflecting intensity vs. seconds

Pressure vs. nm/min.

40°C, 50°C

Cornell University
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Effects of polarity

- Molecules with less than 3 –OH groups still significantly soluble.
- Effect more pronounced at lower temperatures.
- Indicative of contrast between exposed and unexposed regions.
Effect of molecular weight, Tg

- Necessary pressure to achieve dissolution rate increases predictably with larger MW.
- However, photoresists approaching 2000 g/mol still soluble in scCO2!

Going forward

• Methodology in place for predicting, measuring scCO$_2$ solubility, especially with small molecules
  – Patterning possible with high Tg materials

• Can be expanded to positive-tone materials
  – Need chain-scission type resist materials
Calix[4]resorcinarenes


<table>
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<tr>
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<th>Tg (C)</th>
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<tbody>
<tr>
<td>calix-tboc</td>
<td>107</td>
</tr>
<tr>
<td>4hp-calix-tboc</td>
<td>84</td>
</tr>
<tr>
<td>4tb-calix-tboc</td>
<td>110</td>
</tr>
<tr>
<td>4si-calix-tboc</td>
<td>140</td>
</tr>
</tbody>
</table>

Graph showing the relationship between pressure (PSI) and mm/min for different resorcinarenes.
Patterning

- As expected, sub-100nm performance shown with calix[4]resorcinarenes developed in scCO2
De-crosslinking Resists for Positive Tone

- **PMMA is classic example**
  - High resolution e-beam, EUV resist with low LER
  - Problem: low sensitivity

- **Acid catalyzed de-crosslinking**
  - Improved sensitivity
  - Use acetal bonds to crosslink otherwise scCO$_2$ soluble species

[Diagram showing the process of spin coating, annealing, exposure, and scCO$_2$ treatment]
Acetal-backbone polymers

- Optimal system for scCO2 development
  - Bisphenol-type compounds shown to be scCO2-soluble
  - Large changes in molecular weight lead to solubility contrast
Patterning

- Electron-beam patterning, 100kV, Cornell
- Develop in scCO2: 40C, 2000 psi (140 bar)
- First intrinsic positive-tone system for scCO2 development!
Summary

• Along with being environmentally friendly, supercritical CO2 shows performance advantages.

• Molecular glass photoresists have shown good performance, low LER under EUV patterning.

• Any given molecular glass platform has the potential for both base development and scCO2 development.
  – Molecules approaching 2000 g/mol significantly soluble
  – < 65nm features shown with select systems

• First report of intrinsic positive-tone system for scCO2 development.
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