Applications of SCF to Semiconductor Lithography

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Where and How Does a New Process Fit In

- Eliminates Present Process Steps
- Substitute Safer Liquid/Gas for Another
- Solve Process Problem
- Fit New Process to Existing Materials
- Design New Materials to Fit New Process Fluids

Reduce Costs
Improve Yields
Eliminate Waste
Recycle

Lower Cost
PROCESS LIQUIDS for SC LITHO

Clean- H2O2, NH4OH, Organic Solvents

Prime- HMDS or Apply Organic Arc

Apply- Organic Solvents

expose

Develop- TMAH, Organic Solvents

Rinse- Water, SCF, Organic Solvents

"Teflon"like residue

Etch (RIE)- CF4 gas or HF liq

Strip- Organic Solvents
Stages of Conversion of Green Lithography

Apply solvents
Solvent strip
Alkaline developer
Aqueous cleaners

Water rinse

All Water Process Liquids

Reduced Volume of Water

Gas
SCF Liquid

Gas
PROCESS LIQUIDS for SC LITHO

Clean- H₂O₂, NH₄OH

Apply- PGMEA, Ethyl Lactate

Develop- TMAH, Organic Solvents

Rinse- Water, SCF, Organic Solvents

Etch (RIE)- CF₄ gas or HF liq

Strip- NH₂OH, organic solvents
Integration of SCF into Lithography

- Replace SCF anywhere water is used
- Replace SCF anywhere organic solvents used
- Reduce amt of water/solvent and waste
- Displace water/solvents
- Fit the SCF process to existing tools/mtls/process (200-300mm/1min)
- Design mtls/process/tools for SCF integration
Properties of SCFCO2 Used in SemiConductor Processes

- Low Toxicity
- Low Cost
- Critical Point 31°C, 1200 psi
- Lowest Surface Tension Fluid
- Wettability
- High Solvent Power rel Hexane
- High Diffusitivity
- Low Viscosity
- $\text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{H}_2\text{CO}_3$
\[ E(\text{coh}) = E(\text{np}) + E(p) + E(\text{hb}) \]

Co-solvent- Good solvent dilute SCFCO_2

<table>
<thead>
<tr>
<th>Solvent or Polymer</th>
<th>Non Polar</th>
<th>Polar</th>
<th>H Bond</th>
<th>Sol Par</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>7.4</td>
<td>6.0</td>
<td>10.9</td>
<td>13.4</td>
</tr>
<tr>
<td>IPA</td>
<td>7.7</td>
<td>3.0</td>
<td>8.0</td>
<td>10.7</td>
</tr>
<tr>
<td>Propglycol</td>
<td>8.2</td>
<td>4.6</td>
<td>11.4</td>
<td>12.8</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>7.1</td>
<td>3.9</td>
<td>4.6</td>
<td>11.0</td>
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<tr>
<td>NMP</td>
<td>8.8</td>
<td>6.0</td>
<td>3.5</td>
<td>resist strip, 14.8</td>
</tr>
<tr>
<td>Butyl acetate</td>
<td>7.7</td>
<td>1.8</td>
<td>3.1</td>
<td>9.5</td>
</tr>
<tr>
<td>Xylene</td>
<td>8.7</td>
<td>1.0</td>
<td>1.0</td>
<td>9.7</td>
</tr>
<tr>
<td>Hexane</td>
<td>7.2</td>
<td>0.0</td>
<td>0.0</td>
<td>7.2</td>
</tr>
<tr>
<td>SCFCO_2</td>
<td>7.2</td>
<td>0.0</td>
<td>0.0</td>
<td>7.2</td>
</tr>
<tr>
<td>Teflon</td>
<td></td>
<td></td>
<td></td>
<td>6.6</td>
</tr>
<tr>
<td>PMMA</td>
<td></td>
<td></td>
<td></td>
<td>9.3</td>
</tr>
<tr>
<td>Polystyrene</td>
<td></td>
<td></td>
<td></td>
<td>8.6</td>
</tr>
</tbody>
</table>
$p - \rho - T$ Surface of Pure CO$_2$
## Surface Tension of Process Liquids

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Density, g/ml</th>
<th>Viscosity, cps</th>
<th>Surface Tension, mN/m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0.99</td>
<td>0.91</td>
<td>72</td>
</tr>
<tr>
<td>Water/surfactants</td>
<td></td>
<td></td>
<td>20-40</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.85</td>
<td>1.08</td>
<td>22</td>
</tr>
<tr>
<td>t- butyl alcohol(TBA)</td>
<td>0.81</td>
<td>3.5</td>
<td>20</td>
</tr>
<tr>
<td>50/50 TBA/H2O</td>
<td></td>
<td></td>
<td>24</td>
</tr>
<tr>
<td>Fluoroalkane</td>
<td></td>
<td>5-14</td>
<td></td>
</tr>
<tr>
<td>Liquid CO2</td>
<td>0.87</td>
<td>0.08</td>
<td>1.5</td>
</tr>
<tr>
<td>SCF CO2</td>
<td>0.35-0.85</td>
<td>0.03</td>
<td>0</td>
</tr>
</tbody>
</table>

## Interfacial Tension

<table>
<thead>
<tr>
<th>Interface</th>
<th>Surface Tension, mN/m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water/SCF CO2</td>
<td>15</td>
</tr>
<tr>
<td>Water/SCF CO2/Silicone surfactant</td>
<td>2</td>
</tr>
</tbody>
</table>
**EXAMPLE - Silylation in SCF**

\[
\text{OH} + (\text{CH}_3)_3\text{Si}NH(\text{CH}_3)_3 \xrightarrow{\text{HMDS}} \text{OSi(CH}_3)_3 + \text{Me}_3\text{SiNH}_2
\]

<table>
<thead>
<tr>
<th>Sample</th>
<th>CONTACT ANGLE (water drop) deg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare silicon wafer</td>
<td>26</td>
</tr>
<tr>
<td>Silicon wafer silylated by HMDS in Gas Phase YES oven</td>
<td>78</td>
</tr>
<tr>
<td>Silicon Wafer silylated by HMDS in SCFCO2</td>
<td>87</td>
</tr>
<tr>
<td>Glass slide</td>
<td>21</td>
</tr>
<tr>
<td>After silylation</td>
<td>59</td>
</tr>
</tbody>
</table>
REPLACE Aq BASE/water with SCF as DEVELOPER
Reason- avoid image collapse with Low ST SCFCO2 and reduce volumes of dev/water for processing

Challenge-Few Polymers Soluble in SCFCO2 mainly low ST polarity(ST) Fluorocarbons/siloxanes/ethers solubility parameter < 8
May require co-solvent to boost polarity of SCFCO2 Positive resist most difficult
Polar to non polar
Chain Scission
Deposit Resist from by Spin Coating in Liquid CO₂

DEVELOP UNEXPOSED SCF CO₂ SOLUBLE as NEGATIVE RESIST

\[
\text{CH-CH}_2\text{-CH-CH}_2 + \text{CO}_2\text{sol polymer} \rightarrow \text{CH-CH}_2\text{-CH-CH}_2 \text{exposed}
\]

\[
\text{(CF}_2\text{)}_n\text{CF}_3 \text{TBu} \text{CO}_2 \quad \text{OTS} \quad \text{NO}_2
\]

**SPIN COAT**

Apply resist in Liq CO₂ <3000 psi

Expose

unexposed develops off

SCF develop exposed remains

neg
EXAMPLE
POLARITY CHANGE POSITIVE RESIST

Non polar $\rightarrow$ polar
Polar $\rightarrow$ Non polar

Cl

CO$_2$C(CH$_3$)$_3$

Chain Scission

$S = k(M_w)^a$

Polarity of products?

C=CH$_2$ + CH$_2$=C

COOH

+HCl +IB
Example of SCF/Co-solvent Developed EB resist

Cl
\[ \text{Chain Scission} \]
\[ \text{Polarity of products} \]

\[ \text{SCFCO}_2 + \text{Xylene} \]
\[ \text{SCFCO}_2 + \text{Ethanol} \]

\[ \text{SCFCO}_2 \]

\[ \text{SCFCO}_2 + \text{Xylene} \]
\[ \text{SCFCO}_2 + \text{Ethanol} \]

\[ S = k(M_w)^{-a} \]

% Exposed Film Remain after Development

Dose \( \mu \text{c/cm}^2 \)

\[ \begin{align*}
\text{SCFCO}_2 & + \text{Ethanol} \\
\text{SCFCO}_2 + \text{Xylene} &
\end{align*} \]
SILYLATION with SCF - BILAYER (TOP SURFACE IMAGING)

for High Resolution Imaging over Reflective Substrates or Topography
Provide Uniform Silylation over 300 mm diameter wafers

O2 RIE

SiO2

CF4 type RIE Etch
Present Chem Amplified Resist
Aqueous base Developer/water rinse

Example
AR = 3

1990
300 nm L/S by 900 nm thick

2000
150 nm L/S by 450 nm thick

AR = 3

2005
80 nm L/S by 240 nm thick

AR = 3

2010
40 nm L/S by 120 nm thick

Figure 1 - Trends in Resist Feature Sizes
Where Has all The Resist Gone?

Decreasing Depth Focus

THICKNESS of RESIST, nm

1000
900
800
700
600
500
400
300
200
100
0

YEAR

1980 1990 2000 2010

400 nmL/S
150 nm L/S
50 nm L/S

RIE min Thickness
Image Collapse
\[
F = \frac{(St)}{r} \\
W(o) = 4A(\exp+3)F/E \\
W(o) = 4A(\exp+3)(St)/Er
\]

\[
E = \text{Youngs Modulus (GP(a))} \\
\text{Lower (ST) or raise } E
\]

\[
A_r = H/w > 3
\]


- Example of Image Collapse and Early Model
IMAGE COLLAPSE in DRYING DUV RESIST

Surface Tens(H2O) (adhesion Failure(AF))

Collapse = (Pressure)(Aspect Ratio(H/W))
= 2(ST)(H) = \frac{(144d/cm)(500nm)}{1000 \text{ nm} \times 100\text{nm}}

Collapse Force = 7 \times 10^{(exp+7)}\text{dynes/cm}

ADHESIVE BOND STRENGTH = < 1 \times 10^{(exp+7)} \text{d/cm}

USE LOW ST to DRY LIQUID as SC CO2 < 1 \text{d/cm}

USE STIFFEST RESIST (High Shear modulus)
Shear Modulus general increase with T(g)
Highest in X linked mtl(s) (neg resist ?)
**Young's Modulus of Resist Films**

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>E (GPa) +/- 0.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>KRS-XE (PHS)</td>
<td>5.3</td>
</tr>
<tr>
<td>ESCAP KrF resist</td>
<td>5.1</td>
</tr>
<tr>
<td>APEX-KrF PHS</td>
<td>5.1</td>
</tr>
<tr>
<td>Neg(exp) PHS KrF</td>
<td>4.2</td>
</tr>
<tr>
<td>Acrylate ArF</td>
<td>3.9</td>
</tr>
<tr>
<td>COMA ArF</td>
<td>2.6</td>
</tr>
<tr>
<td>CO ArF</td>
<td>2.6</td>
</tr>
<tr>
<td>ZEP e beam</td>
<td>2.2</td>
</tr>
</tbody>
</table>

PHS - Polyhydroxystyrene, ESCAP-PHS-co-tbutylacrylate, COMA - Cyclic olefin/maleic anhydride, EB-ebeam, ZEP-Nippon Zeon - Poly co-chloroacrylate/methylstyrene, APEX Shipley PHS type; SAW by Dr. Thomas Schuelke, Fraunhofer USA, Bradley Univ, Peoria, Illinois.
Fig. 2- Methods of Image Collapse Reduction

a-Dry Develop  b-f (lower St)  g-157nm SCF resist
Super Critical Fluid for Prevention of Image Collapse

- **Solvents Highly miscible in scCO2**
  - Acetic Acid
  - Methanol
  - IPA
  - Toluene
  - Ethanol
  - **Fluorinated Solvents and polymers > 40 % F by wt and fluorosurfactants**
  - Polysiloxane
  - cyclic cpds such as ethers,lactones

- **Not miscible in scCO2 - < 0.1 grams/100 grams**
  - Water
Water Removal Directly on 193 nm Resist
Under SCF 65C, 4500 psi
EXAMPLES of CO$_2$ Phillic SURFACTANTS

\[ \text{Me}_3\text{SiO(Me}_2\text{SiO)}_x\text{MeSiO}_{y}\text{SiMe}_3 \]

\[ \text{CH}_3(\text{CH}_2\text{CH}_2)_x-(\text{CH}_2\text{CHCH}_2\text{O})_y\text{CH}_3 \]

\[ \text{CF}_3(\text{CF}_2\text{CF}_2)_n\text{CF}_2\text{CF}_2\text{COOH} \]

\[ \text{CH}_3 \quad \text{CH}_3 \]

\[ \text{HO(CH}_2\text{CH}_2)_x-(\text{CH}_2\text{CHO})_y-(\text{CH}_2\text{CHO})_z\text{-OH} \]

\[ \text{CH}_2\text{CBOHCHCOHCH}_2\text{OH} \]
SCF CO2 Drying of Resist to Prevent Image Collapse

Positive CA Resist  TMAH Dev, H2O rinse
800 nm thick 150 nm images , Aspect ratio = 5

control

SCF dry
Sets of pairs of Apex-E lines were written using a Leica Cambridge EBMF 10.5 ebeam.

**APEX-E line** processed using \textit{scCO}_2

and surfactant AOT

- linewidth = 130 nm
- spacing = 370 nm
- Aspect ratio = 7.3
- L/S = 1 : 2.8
- magnification = 20K

Same sample after rewetting in \textit{hexane} and normal dried.

Figure 6-APEX-E, AR = 7, AOT/Hexane Rinse, SCF CO2 dry
## Solvent Resistance of NEG CAR RESIST

<table>
<thead>
<tr>
<th>SOLVENT</th>
<th>ATTACK</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>Severe- 20 % film loss</td>
</tr>
<tr>
<td>Ethanol</td>
<td>Severe</td>
</tr>
<tr>
<td>Isopropyl alcohol IPA</td>
<td>Slight- 2 % film loss</td>
</tr>
<tr>
<td>Butanol</td>
<td>moderate</td>
</tr>
<tr>
<td>Acetone</td>
<td>Severe</td>
</tr>
<tr>
<td>Methoxyproponal</td>
<td>Stripped</td>
</tr>
<tr>
<td>Ethyl lactate</td>
<td>Severe</td>
</tr>
<tr>
<td>Glacial acetic acid</td>
<td>Moderate</td>
</tr>
</tbody>
</table>
Figure 7-a, 90 nm lines CGR AR=5, Water/SCF CO2 dry

b, 90 nm lines, CGR AR=5, Water/IPA/SCF CO2 dry
Figure 4-a, 100nm, AR=4, KRS-XE, Water rinse, air dry

Figure 4-b, 100 nm, AR=6, KRS-XE, Surf Rinse, air dry
## ASPECT RATIO ACHIEVEMENTS in Solving Image Collapse

<table>
<thead>
<tr>
<th>Line/space,</th>
<th>Aspect Ratio</th>
<th>AR/LS</th>
<th>Resist</th>
<th>Process</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>20/20 nm</td>
<td>7</td>
<td>0.35</td>
<td>ZEP (PO)</td>
<td>SCF dry</td>
<td>Namatsu</td>
</tr>
<tr>
<td>50/120 nm</td>
<td>6</td>
<td>0.12</td>
<td>NEB-31(NA)</td>
<td>Surf/Liq/SCF</td>
<td>Namatsu</td>
</tr>
<tr>
<td>80/80 nm</td>
<td>5</td>
<td>0.07</td>
<td>ZEP (PO)</td>
<td>Perflhex dry</td>
<td>Yamashita</td>
</tr>
<tr>
<td>50 nm/50 nm</td>
<td>6</td>
<td>0.06</td>
<td>157 nm (PS)</td>
<td>SCFdev/dry</td>
<td>someday</td>
</tr>
<tr>
<td>100/100 nm</td>
<td>6</td>
<td>0.06</td>
<td>KRS-XE (PA)</td>
<td>Surf/H2O Rin</td>
<td>This work</td>
</tr>
<tr>
<td>140/370 nm</td>
<td>7</td>
<td>0.05</td>
<td>APEX (PA)</td>
<td>Surf/Hex,SCF</td>
<td>Goldfarb</td>
</tr>
<tr>
<td>150/250 nm</td>
<td>6</td>
<td>0.04</td>
<td>KRS-XE(PA)</td>
<td>H2O/SCF dry</td>
<td>This work</td>
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<tr>
<td>200/200 nm</td>
<td>5</td>
<td>0.03</td>
<td>PN 100 (NA)</td>
<td>TBA/H2O Rin</td>
<td>Tanaka</td>
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<tr>
<td>130/130 nm</td>
<td>3.5</td>
<td>0.03</td>
<td>COMA (PA)</td>
<td>H2O Rinse</td>
<td>Cao</td>
</tr>
</tbody>
</table>

**PO** - Pos organic dev resist  
**NA** - Negative Aqueous based resist  
**PA** - Positive Aqueous Based Resists  
**PS** - Positive SCF develop
SCFCO2 CONSIDERATIONS/Water Removal

- Surfactant Required and Is it Inert to Resist
- Remove Water Prior to SCF Dry?
- Time to Dissolve Rinse Solvent in SCF
- Press/Temp of SCF Reactor
- Rate of Depressurization
IMAGE COLLAPSE

- Aspect Ratio > 3 < 150 nm L/S = IC
- Lower ST of Rinse/DRY Effective
- Removal Of Rinse Water Challenge in PR
- Remove Water by Inert Liquids followed by SCFCO2 Dry Shows Promise
- Future Challenges in Overcoming IC

Positive Resists "Insolubility"
Tool Design/Process Throughput
SCF Developable Resist
Cleaning Applications for SCF

On Surface

DISSOLVE OFF
DISPLACE
DISLODGE
SWELL
EMULSIFY
UNDERCUT
CHEMICAL CONVERSION

In trench

Strip vs Etch vs Clean

Residue or Film
Type- Polymeric
Organic/inorganic/Metallic/mixed
RIE Residue Removal.

Al structure post RIE

After clean w/CO₂
Post CMP Residue Removal.

- $\text{CO}_2$
- $\text{CO}_2 + \text{CoSolvent C}$
TOWARD ALL GAS PHASE LITHO

- Stage 1 - Eliminate/Reduce Organic Solvents by Aqueous Strip
- Stage 2 - Eliminate/Reduce Aqueous Liquids by SCF Process in Clean/strip and Deposit and develop/dry
- Stage 3 - All Gas Phase Lithography monomer example octavinyilsilsesquioxane.

Clean → Expose → RIE Etch → Strip

Deposit/monomer or polymer in bilayer type resist or on hard mask

Develop by heat or RIE gas or SCF

Millions gal

lbs/liters gas
Example - Dry Lithography

Cycloalkylvinylsiloxane monomer

Vac deposit → Expose

SCF → Heat vaporize
SUMMARY of SCF FLUID LITHOGRAPHY

1. Clean - SCF + (COSOLVENT + surfactant)
2. Prime - HMDS/SCF
3. Apply - 157nm/SCF
4. Expose
5. Silylation in SCF
6. Develop - SCF/(co-solvent + surf)
7. O2 RIE develop
8. Rinse -
9. "Teflon" like residue (CF2-CF2)n
10. Etch (RIE) - CF4 gas or HF liq
11. Strip - SCF + (Co-solvent + surf)
SUMMARY of SCF applied to Semiconductor Lithography

- Can it replace/displace water based process
- Can it replace/reduce organic solvents
- Can it fit into into existing process
- Initial Feasibility in cleaning and drying
- New Applications
- Future Integrate
Acknowledgements

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