Using scCO$_2$ and Cosolvents for Microelectronics Processing

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In collaboration with
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Outline

• Review of Supercritical Fluids (SCF)
  – Supercritical CO\textsubscript{2} (scCO\textsubscript{2}) and SCF properties
  – Reasons for interest in semiconductors (2 examples)

• Adding organic solvents to scCO\textsubscript{2} solutions
  – Effects

• Ober Group CO\textsubscript{2} System with Cosolvent Capabilities
  – Specifications

• Using scCO\textsubscript{2} and scCO\textsubscript{2} + cosolvent to develop photoresists
  – MIT/Cornell chemical vapor deposition (CVD) resist project
Outline (Continued)

• Difficulties / Concerns
  – Effects
  – Rationale for choosing cosolvent

• Conclusions / Outlook
  – Closing remarks
  – Acknowledgements
Why Consider Alternative to Organic Solvents?

- The semiconductor industry has been growing at an annual rate of about 15% over the last thirty years.
- Typically, a semiconductor processing line that produces 5000 wafers per day will generate 8000 liters of waste solvent and 8000 liters of contaminated rinse water per day.*
- These contaminated organic and aqueous solvents are environmentally unfriendly and costly to recover and dispose of.

Supercritical CO₂ (scCO₂)

• CO₂ is inexpensive and it has a moderate critical point: T_c (31.1 °C) and P_c (1070 psi). Non-flammable and non-corrosive.

• Gas-like diffusivity and viscosity, but liquid-like density.

  • Low viscosity and near zero surface tension.
  • No dipole moment, but a very large quadrupole moment.
Supercritical Fluids vs. Gases and Liquids

- Order-of-magnitude comparison of physicochemical properties of a typical gas, liquid, and a supercritical fluid (SCF)

<table>
<thead>
<tr>
<th>Property</th>
<th>Gas</th>
<th>SCF</th>
<th>Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (kg/m³)</td>
<td>1</td>
<td>700</td>
<td>1000</td>
</tr>
<tr>
<td>Viscosity (g/cm s)</td>
<td>$10^{-5}$</td>
<td>$10^{-4}$</td>
<td>$10^{-3}$</td>
</tr>
<tr>
<td>Diffusion Coefficient (cm²/s)</td>
<td>$10^{-1}$</td>
<td>$10^{-4}$</td>
<td>$10^{-5}$</td>
</tr>
</tbody>
</table>
Environmental Benefits of scCO$_2$

- CO$_2$ is naturally occurring and readily available (as a by-product from the production of other compounds.)
- When released into the atmosphere, liquid CO$_2$ leaves no residue to contaminate the environment or personnel.
- Processes that use CO$_2$ do not add directly to the greenhouse effect.
- CO$_2$-based processes can be more energy efficient than those based on water or conventional solvents since CO$_2$ has a low heat of vaporization.
- Approved by the EPA as a non-ozone-depleting chemical alternative.
Processing Benefits: Preventing Pattern Collapse

H$_2$O

CO$_2$

scCO$_2$ MEMS Drying Device

- CO$_2$ exchange displaces water or polar solvents
- Elimination of capillary forces

H. Namatsu, K. Yamakazi, K. Kurihara
Microelectronics Engineering, 46 (1999)
Effect of Cosolvents on Supercritical CO$_2$ Mixture

• Since CO$_2$ is not polar, polar solutes do not dissolve in scCO$_2$.

• Adding a small volume of a polar cosolvent can dramatically improve the solubility of a polar solute in scCO$_2$ thanks to interactions between the cosolvent and the solute.

• By adding cosolvents, we are affecting the thermodynamics of the mixture. Generally, these thermodynamic interactions are complicated.
Mixed Solvent Processing

Solvent Pump  scCO₂ System
SCF Processing Vessel at Cornell

- Manufactured by Supercritical Fluid Technologies (Newark, DE)
Introducing Cosolvents:
The Ober Group Supercritical Fluid Technologies SFT-150

- Cosolvents are pumped into the system using a HPLC pump.
- $\text{CO}_2$ mixes with the cosolvent before passing through diffuser plates and into the processing vessel.
The Gleason group at MIT has been working on a system of *hot filament CVD* that can deposit uniform polymer films onto Si wafers.

The polymer used in this collaboration is poly(glycidyl methacrylate) – a known high-speed electron-beam (e-beam) resist.

Incident electrons induce a crosslinking reaction in the polymer film.

As is, poly(glycidyl methacrylate) is a negative-tone (exposed area remains after developing) resist system.
Hot Filament CVD of GMA

- Precursor GMA 3 sccm
- Energy input: 3.2 W
- Temperature: 200 ~ 240 °C

- Rapid deposition rate: >3,000 Å/min
- RMS roughness: <2 nm
- Thickness variation: <2 %
- MW range: 20K–120K

- thermal generation of growth species.
- low-energy process, low filament temperature.
- no UV irradiation and ion bombardment.
- control over reaction pathways.
- material utilization efficiency ~10%.
Crosslinking pGMA

\[
\text{e-} \quad \text{e-} \quad \text{develop}
\]

resist
wafer

\[
\text{H}_2\text{C} - \text{CH}_3 \\
\text{C} - \text{C} \\
\text{O} - \text{O} \\
\text{H}_2\text{C} - \text{CH} \\
\text{H}_2\text{C} - \text{O}
\]

\[
\text{H}_2\text{C} - \text{CH}_3 \\
\text{C} - \text{C} \\
\text{C} - \text{O} \\
\text{H}_2\text{C} - \text{CH}_3 \\
\text{C} - \text{O} - \text{O}
\]

\[
\text{H}_3\text{C} - \text{C} - \text{O} - \text{R}
\]
Results with pGMA

- As expected, the polymer is insoluble in scCO₂.
- Adding 2 vol% CH₂Cl₂ allows for some patterns to be developed.
Methods of Improving the Resist

- Adding fluorine containing groups to the polymer has the potential of dramatically improve the solubility in CO₂.

\[
\begin{align*}
\text{CH}_3 \quad \text{H}_2 \quad \text{C} - \text{C} \quad \text{O} \quad \text{O} \\
\text{C} - \text{C} \quad \text{H}_2 \quad \text{H} \quad \text{C} - \text{C} \\
\text{O} \quad \text{O} \\
\text{CH}_2 \quad \text{CH}_2 \quad (\text{CF}_2)_5 \quad \text{CHF}_2
\end{align*}
\]
FA-GMA Copolymer

CVD GMA-FA film, SCF CO₂ (n = 35, m = 65)
CVD GMA-FA film, SCF CO₂ + 2% EtOH
CVD GMA film, SCF CO₂ (n = 63, m = 37)

SCF CO₂ condition: 45 °C, 10~15 mins.
FA-GMA Copolymer (continued)

P = 6000 psi, T = 45 °C, t = 10 min
n = 35, m = 65
How We Chose the Cosolvent

• Choosing cosolvents is sometimes complicated……..

<table>
<thead>
<tr>
<th>Cosolvent</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrahydrofuran</td>
<td>Film Removed</td>
</tr>
<tr>
<td>Methylene Chloride</td>
<td>Film Removed</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>No Effect</td>
</tr>
<tr>
<td>Acetone</td>
<td>No Effect</td>
</tr>
<tr>
<td>Ethanol</td>
<td>No Effect</td>
</tr>
<tr>
<td>Methanol</td>
<td>No Effect</td>
</tr>
</tbody>
</table>

This leads us to the next point…
An Alternative to Cosolvents: Specific Surfactants

- Specifically designed organic surfactants have been used as additives to scCO₂. For example:

Difficulties / Concerns

• Although there do exist methods of calculating solute solubility in SCFs, these methods may be cumbersome and impractical to apply to polymers.
• Qualitative methods do exist (GC column, solubility triangle, etc.) but they have limitations of their own.
• A rapid screening technique / predictive tool would be a great boon to the art of supercritical fluid processing / extraction.
• Some of the cosolvents that are being used are still not optimal. Cosolvents that are truly environmentally benign may not be effective.
A Look at an Ongoing Project: Replacing the Ashing Step with scCO$_2$

- The ashing step in a semiconductor plant is required to remove residual resist, barc, etc. from the wafer after etching.
- Is it possible to replace this ashing step with CO$_2$ and a cosolvent / surfactant?

Image courtesy of Phil Matz, Texas Instruments.

Sample pattern that has been etched, but not ashed. Magnification of 100X.
Outlook and Conclusions

• scCO$_2$ is a unique solvent that embodies many of the qualities that manufacturing may be interested in.
• By adding small volumes of cosolvents, the thermodynamic properties of a SCF mixture can dramatically change.
• We has shown that scCO$_2$ and cosolvents can be used together in order to develop a negative-tone photoresist.
• Conditions have yet to be optimized, and an improvement in resolution is expected in the near future.
Acknowledgements

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