SCORR - Supercritical Carbon Dioxide Resist Removal

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Submitted to:
3rd International Conference on Microelectronics and Interfaces, Santa Clara CA, Feb 12-14, 2002
SCORR, short for supercritical carbon dioxide resist removal, is a new technology that could continue to enable the technological development of photolithography processes in industry. SCORR is based upon the physical properties of supercritical fluids (SCFs). These special properties enable SCFs to remove coatings, residues, and particles from high-aspect-ratio structures in integrated circuits (ICs). SCORR also eliminates rinsing and drying steps presently used in IC manufacture, thereby eliminating the generation of millions of gallons of water per fab per day.

Fabricating integrated circuits relies heavily on photolithography to define the shape and pattern of individual components. Once a single stage of a silicon wafer’s topography has been completed, the hardened resist must be removed. Conventional processes generates more waste than any single step in the IC manufacturing process, and the production of a complete IC can involve many photolithography iterations. The cost associated with the treatment and disposal of this waste, as well as employee health and safety considerations, are driving a search for alternative, environmentally benign, cost-effective solutions.

In addition, photoresist stripping is confronting finer architectures and higher aspect ratios, as well as new low-k materials that are highly sensitive to post-etch residue. Low-k dielectrics and low-resistivity conductors such as copper are necessary for meeting industry’s need for faster and smaller chips. Further, each low-k choice requires different plasma-etching processes, or chemistries, to etch structures into the low-k material; therefore, the nature of the residues can be different. No one product can meet all copper/low-k applications, and existing chemistries are not tunable—or even desirable—for the new processes.

We have developed a new process—known as SCORR—that removes photoresist and post-ash, -etch, and -CMP (particulate) residue from semiconductor wafers. As IC feature sizes become smaller, the need for ensuring particle removal will increase. With feature sizes of less than 0.18µm, it will become imperative that all particles greater than about 0.1 micron be removed from the semiconductor wafer. Existing cleaning technologies (such as liquid or high-pressure jet scrubbing) cannot remove particles on the order of 0.1 micron because of surface boundary layer constraints. Because of the low viscosities of supercritical fluids (SCFs), these constraints are virtually eliminated.

The key to the effectiveness of SCORR is the use of SCFs, specifically supercritical carbon dioxide (CO2). The physical properties (e.g., density, viscosity, diffusivity) of a supercritical fluid often lie between those of gases
and liquids, and can be varied by small changes in temperature and/or pressure.\(^1\)

Fig. 1. Carbon dioxide density as a function of temperature and pressure.

The possibility to obtain a wide range of physical properties without changing the chemical composition and by using a fluid than becomes gaseous at atmospheric pressure, makes these fluid attractive for a wide range of applications.\(^2\) Carbon dioxide is generally chemically inert with respect to inorganic materials and is therefore compatible with existing semiconductor materials and metallization systems. Supercritical fluids have, by definition, no surface tension which offers the possibility for the removal of very small (sub-micron) particles from substrate surfaces.\(^3\) They are therefore ideal candidates for the removal of photoresist from fabricated surface structures having high aspect ratios. Carbon dioxide is noncombustible, readily available in high purity, environmentally friendly (not ozone depleting), and has a low human toxicity.

Pure supercritical CO\(_2\) is limited in its ability to dissolve most polymers (photoresists).\(^4\) Rather, it is the absorption of supercritical CO\(_2\) into the polymer and the resulting swelling of the polymer that can be utilized to achieve various desirable interactions. By “tuning” the CO\(_2\)/polymer interaction with pressure and temperature adjustments, supercritical CO\(_2\) is absorbed into the polymer-based photoresist, thus plasticizing the polymer and lowering its glass transition temperature significantly below that observed at atmospheric pressure. Lowering the polymer’s glass transition temperature softens it, thereby enhancing penetration and speeding the diffusion of the supercritical fluid into the polymer/substrate interface.\(^5\) The principle is to swell the polymer with the dense gas, allowing the supercritical CO\(_2\) to diffuse throughout the polymer matrix and then suddenly release the pressure, forcing a rapid volume change that ruptures the polymer from the substrate.\(^6\)

To further enhance solubility or overcome bonding effects, a second compound, or co-solvent, is added to the supercritical CO\(_2\). The high densities achievable in the SCF region provide the necessary solvating power to solubilize small amounts of co-solvent (less than 5% by volume), which then can diffuse throughout the polymer matrix and to the polymer/substrate interface. This diffusion provides for significant chemical interaction, which promotes the photoresist and residue removal.

Supercritical CO\(_2\) is also attractive from the viewpoint of waste minimization. After the cleaning step, CO\(_2\) is easily separated from the extracted or dissolved compounds, resulting in streams of concentrated compounds and pure, recyclable CO\(_2\). Because SCORR uses pure CO\(_2\) for its
final rinse step, it does not deplete critical water reserves. SCORR’s solvent system is not only nontoxic but also recyclable, and thus the only waste generated is the spent solubilized photoresist, which is itself non-regulated. And finally, instead of using alcohol for the drying process, we merely lower the pressure and temperature of the supercritical CO₂, and thus the supercritical fluid returns to its gaseous phase, leaving the silicon wafer dry and virtually free of any residue.

The SCORR system is a technology based on sound green chemistry principles while enabling the industry to meet its development goals, such as the introduction of low-k dielectric materials, which are sensitive to the established chemistries, plus copper and smaller line widths. The SCORR system chemistry and instrumentation will be presented in detail. Advantages of the SCORR system to the industry and the environment will also be discussed.

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SCORR
Supercritical CO$_2$ Resist Removal

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SCORR

Cleaning Fluid:

$\text{CO}_2 + 1-3 \text{ wt\% cosolvent at supercritical conditions.}$

Benefits

- Compatible with higher aspects ratios ($<0.10 \ \mu m$)
- Compatible with low-k materials
- Removes photoresist, post-ash, -etch and CMP residues
- Eliminates DI water rinse step
- Eliminated IPA dry step
- Reduces hazardous chemcials
- Recycle $\text{CO}_2$
Future Applications in IC Manufacturing

- Wafer cleaning
- Film deposition
- Film etching
- Photoresist developing
- Photoresist stripping
- Residue removal
- Drying (MEMS)
- Particulate removal
- Waste treatment
Supercritical Fluids

<table>
<thead>
<tr>
<th>Fluid</th>
<th>$T_c$ (°C)</th>
<th>$P_c$ (psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne</td>
<td>-229</td>
<td>400</td>
</tr>
<tr>
<td>N$_2$</td>
<td>-147</td>
<td>492</td>
</tr>
<tr>
<td>Ar</td>
<td>-122</td>
<td>706</td>
</tr>
<tr>
<td>Xe</td>
<td>17</td>
<td>858</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>31</td>
<td>1072</td>
</tr>
<tr>
<td>SF$_6$</td>
<td>46</td>
<td>545</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>97</td>
<td>617</td>
</tr>
<tr>
<td>NH$_4$</td>
<td>133</td>
<td>1654</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>374</td>
<td>3209</td>
</tr>
</tbody>
</table>

- **Solid**
- **Liquid**
- **Supercritical CO$_2$**
- **Gas**

<table>
<thead>
<tr>
<th>Property</th>
<th>Liquid</th>
<th>SCF</th>
<th>Gas</th>
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</thead>
<tbody>
<tr>
<td>Density (g/cm$^3$)</td>
<td>1</td>
<td>0.1-0.5</td>
<td>10$^{-3}$</td>
</tr>
<tr>
<td>Viscosity (Pa-s)</td>
<td>10$^{-3}$</td>
<td>10$^{-4}$ - 10$^{-5}$</td>
<td>10$^{-5}$</td>
</tr>
<tr>
<td>Diffusivity (cm$^2$/s)</td>
<td>10$^{-5}$</td>
<td>10$^{-3}$</td>
<td>10$^{-1}$</td>
</tr>
</tbody>
</table>
Pure Fluid PVT Surface

Supercritical fluids are attractive solvents because of

- high diffusivity
- low viscosity
- zero surface tension
- tunable solvent strength
- nontoxic
- recyclable
Supercritical Fluid Facility at LANL

Open user facility for applied research

Bench scale to production scale pressure vessels (5 mL – 60 L)

Applications: Weapon parts cleaning
Dry cleaning (Drywash)
Materials modification
Synthesis
Biotechnology
Extraction / separation
Alternative / replacement solvents
Supercritical Fluid Process

![Diagram of supercritical fluid process with a phase diagram showing pressure, temperature, and state phases: solid, liquid, and gas. Key components include a liquid CO₂ container, a pump, a CO₂ recycle line, a heating unit, a cooling unit, a separator, and a treatment vessel. The diagram illustrates the path of the fluid through these components.]
Supercritical Fluid Facility at LANL

High-Pressure Equipment Bay

10-Liter High-Pressure Vessel
Commercial Applications

- The concept of SCF’s as an industrial solvent has grown out of commercial SCF extraction and purification applications

- Decaffeinating coffee
- Production of hops extracts
- Food processing
- Various processes in the petrochemical industry (ROSE process, tertiary oil recovery)
- Dyeing fibers
- SCWO
Photoresist Removal

- Few polymers are soluble in CO₂
- CO₂ is absorbed into many polymers at high pressures

Therefore, unlike wet chemical cleaning, coatings removal with SCF’s does not rely on the dissolution of the polymer coating in the solvent, but rather the dissolution of the SCF solvent in the polymer, and the resulting swelling, to effect its removal.
Polymer – SCF Interactions

Applications requiring polymer solubility in the SCF
- Polymerization
- Fractionation
- Selective Extraction

Applications requiring SCF solubility in the polymer
- Plasticization
- Crystallization
- Selective Extraction
  
  *Coatings Removal*
Polymer – CO$_2$ Interactions

Factors which affect polymers ability to solubilize CO$_2$:

- chemical structure
- polymer crystallinity
- amount of crosslinking
- solubility parameter ($\delta$) match

How do you calculate $\delta$?  
How do they change with T and P?  
How do they change when adding cosolvent?
Solubility Parameters

The Hildebrand solubility parameter, $\delta$, is defined as

$$\delta^2 = \left( \frac{\Delta E}{V} \right)$$

where $E$ is energy of vaporization to the gas at zero pressure, i.e. infinite separation of the molecules, $V$ is the molar volume, and $\left( \frac{\Delta E}{V} \right)$ is the cohesive energy density.
Solubility Parameters for SCF

\[ \delta \text{ can also be expressed as a function of } P_c \]
Giddings approximation:

\[ \delta = 0.47 P_c^{1/2} \rho_r^{\text{SCF}} \]

**CO}_2\ Equation of State (Huang, F.E., Li, M.H., Lee, L.L.,
and Starling, F.T., J. of Chemical Eng. of Japan, 1984)**

\[
P = \rho RT \left[ 1 + b_2 \rho + b_3 \rho^2 + b_4 \rho^3 + b_5 \rho^4 + b_6 \rho^5 + b_7 \rho^6 \exp(-c_{21}\rho^2) + b_8 \rho^7 \exp(-c_{21}\rho^2) 
+ c_{22} \rho^2 \exp(-c_{27}(\Delta T)^2) + c_{23} \frac{\Delta \rho}{\rho} \exp(-c_{25}(\Delta \rho)^2 - c_{27}(\Delta T)^2) 
+ c_{24} \frac{\Delta \rho}{\rho} \exp(-c_{26}(\Delta \rho)^2 - c_{27}(\Delta T)^2) \right]
\]
1-Parameter Solubility Values

\( \text{CO}_2 \)
Hansen Solubility Parameters

HSP

• Improved 3 parameter model

\[ E = E_d + E_p + E_h \]

• Assumes the total cohesive energy density (E) is made up of

- \( E_d \) nonpolar (dispersion) interactions
- \( E_p \) polar (dipole-dipole, dipole-induced dipole) interactions
- \( E_h \) hydrogen bonding (also Lewis acid-base) interactions

\[ \delta_T^2 = \left( \frac{E_d}{V_m} \right) + \left( \frac{E_p}{V_m} \right) + \left( \frac{E_h}{V_m} \right) = \delta_d^2 + \delta_p^2 + \delta_h^2 \]

HSP's
HSP for \( \text{CO}_2 \)

HSP values for \( \text{CO}_2 \) calculated at 25\(^\circ\)C

\[ \delta_d = 15.6 \, \text{MPa}^{1/2} \]
\[ \delta_p = 5.2 \, \text{MPa}^{1/2} \]
\[ \delta_h = 5.8 \, \text{MPa}^{1/2} \]

Values change with T and P
Finding Solubility Parameters

Fig 5-11
Binary Interactions

- If CO₂ HSP cannot match polymer HSP then add a cosolvent
- Calculate solvent-cosolvent HSP using a volume average model
Polymer Swelling in CO₂

CO₂ sorption into polymer lowers $T_g$

Swelling is increased if $T_g$ is exceeded

Swelling decreases polymer/polymer interactions and therefore reduce the δ

Additional polymer/polymer interactions can be reduced by a cosolvent

Depressurization cracks polymer before Polymer/polymer interactions are reestablished.
Photoresist Removal

- Photoresists usually has higher HSP than CO₂
- Increase CO₂ HSP by
  adding cosolvent
  increasing P
  lower T
- Find T condition above $T_g$ but below $T_{mp}$ to increase polymer swelling.
CO$_2$ soluble surfactants

- PFPE (anionic)
  \[
  \text{CF}_3\text{—(OCF}_2\text{CF})_3\text{—OCF}_2\text{—CO}^-\text{NH}_4^+
  \]
  

- PBO-PEO (nonionic)
  \[
  \text{HO—(CH}_2\text{CHO)}_{12}\text{—(CH}_2\text{CH}_2\text{O)}_{15}\text{—H}
  \]
  \[
  \text{CH}_2\text{CH}_3
  \]

- Lodyne 106A (cationic)
  \[
  \text{C}_6\text{F}_{13}\text{—S—OH}
  \]
  \[
  \text{N}^+(\text{CH}_3)_3\text{Cl}^-
  \]
Interfacial Tension

CO$_2$-water-PFPE

T = 45 °C
P = 276 bar
Residue Removal

Exact sidewall polymer composition
Unknown, "fluorinated residue"

3.7 % v/v Butylene carbonate
2900 psi, 85 °C
- Remove via veil and clean the Cu contact surface ($\text{CuO}_x$, F, C)
- Low-$k$ material is $\text{SiO}_2$
- Via size is 0.25 $\mu$m, depth of via is $\sim$ 0.5 $\mu$m
- Static conditions in $\text{CO}_2$-$\text{NH}_3$ (95/5 V%), 30 min, 40°C.
FTIR spectra blanket low-k film

Conditions: Co-solvent: Butylene Carbonate, 2900 psi, 90°C, 7 min

Conclusion: Treatment does not change low-k film
The Arroyo® System

- Cluster tool configuration
- Sold by SC Fluids / GT Equipment
Acknowledgement

LANL
Craig Taylor
Gunilla Jacobson
Kirk Hollis
Laurie Williams
Jerry Barton
Leisa Davenhall
Jim Rubin
Timothy H. Pierce

SC Fluids
Kedar Gupta
Laura Rothman
Ray Robie

Agilent Technologies Inc
Karl Tiefert