Design of Transparent Fluoropolymer Resists for Semiconductor Manufacture at 157 nm

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Outline

• Introduction to microlithography
  – Process technology
  – Materials needs
• Why fluoropolymer photoresists?
• Design of our fluoropolymer platform for 157 nm imaging
• Polymer synthesis issues
• Imaging results
• Extensions and future directions
Photoresists for Microlithography

Materials Employed by the Semiconductor Industry to Create Patterns on the Silicon Wafers Which Will Become Computer Chips.

Spin Coat

Expose

Develop

Dry Etch

Strip
Photoresist Ingredients

- Polymeric Binder
- Photoacid Generator (PAG)
  - Captures Light to Generate Protons which Create Pattern
- Dissolution Inhibitor (DI)
  - Low MW Additive(s) to Increase Contrast
- Adhesion Promoters, Surfactants, Bases, Etc.
Image Formation (248 nm)

- Chemical Amplification: Deprotection Catalyzed by Protons
Etch Rate $\propto \frac{\# \text{ of Atoms in Monomer}}{\# \text{ Carbon Atoms} - \# \text{ Oxygen Atoms}}$

$\Rightarrow$ Need high C/H ratio for good etch resistance
$\Rightarrow$ Aromatic or Polycyclic Groups
Photoresists for Microlithography

- Semiconductor Industry Driven by Miniaturization of Feature Size
  - Proportional to Wavelength of Light

<table>
<thead>
<tr>
<th>λ (nm)</th>
<th>365</th>
<th>248</th>
<th>193</th>
<th>157</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum Feature Size (nm):</td>
<td>180</td>
<td>130</td>
<td>100</td>
<td>70</td>
</tr>
</tbody>
</table>

Source: Hg i-line, KrF Laser, ArF Laser, F₂ Laser
Photoresists for Microlithography

• New Wavelength Nodes Require New Binder Polymers
  – Light Should be Absorbed by PAG, Not Binder Polymer
    • Avoid Binder Decomposition and Outgassing
      » 157 nm = 180 Kcal/Mole
    • Use Light Efficiently
    • Allow Light to Penetrate to Bottom of Film for Straight Sidewalls
      » Absorbance < to << 2.0 µm⁻¹

• Transparency / Thickness Tradeoff
  – Thinner Films Can be More Absorbing but May Have More Defects and Less Etch Resistance
Polymer Binder Properties

- Functionality for image formation and subsequent dissolution in aqueous base
- Transparent at imaging wavelength
- Etch resistant
- High contrast
- Stable at processing temperatures (high Tg)
- Soluble in selected organic solvents for spin coating
- Right molecular weight for proper dissolution behavior
- Adhere to silicon or other substrates
- Suitable for commercial production
- Very pure (ppb metals)

Property conflicts, e.g. Transparency vs. Etch Resistance

Program Goal: Develop new polymer(s) with transparency at 157 nm, chemically amplified imaging, aqueous development and all other properties required for application as photoresist binder
Why Fluoropolymers?

Transparency at 157 nm!

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Absorbance at 157 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyacrylic acid</td>
<td>11.00</td>
</tr>
<tr>
<td>Polynorbornene</td>
<td>6.80</td>
</tr>
<tr>
<td>Polyhydroxystyr ene</td>
<td>6.25</td>
</tr>
<tr>
<td>Polymethyl methacrylate</td>
<td>5.69</td>
</tr>
<tr>
<td>Polyvinyl alcohol</td>
<td>4.16</td>
</tr>
<tr>
<td>Polydimethylsiloxane</td>
<td>1.61</td>
</tr>
<tr>
<td>Teflon®AF (amorphous perfluoropolymer)</td>
<td>0.70</td>
</tr>
<tr>
<td>Polyhydrosilsequioxane</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Kunz et. al. J. Vac. Sci. Technol. 1999, 17, 3267

- All known photoresist platforms were too opaque for use as single layer resists at 157
- Only fluoropolymers and selected silicon polymers promise good transparency
Fluoropolymer Photoresist?

Teflon® AF

- High Tg (165 - 330 °C), Excellent Thermal Stability 😊
- Amorphous and Very Transparent 😊
- Very Hydrophobic 😞
- Soluble Only in Perfluorinated Solvents 😞
- No Functionality for Image Formation 😞
- Poor Etch Resistance 😞

⇒ Design Polymer which Retains First Two, Corrects Last Four
Evolution to a Fluorinated Photoresist

- Excellent transparency ($A = 1.30 \, \mu m^{-1}$)
- Good etch resistance
- $T_g = 150 \, ^\circ C$
- Amorphous, soluble in organic solvents
- Need functionality for imaging

- Adding enough tert-alkyl ester for imaging and aqueous development pushes absorbance above 3.0 $\mu m^{-1}$

- Fluoroalcohols are acidic and transparent
- Readily protected as, e.g. methoxymethyl ether
- Outstanding transparency ($A = 0.7 \, \mu m^{-1}$)
- Some loss in etch resistance
- Dissolves in aqueous base but dissolution rate too slow
Fluorinated Photoresist
(Generation 1)

Etch Resistance

Transparency

Optional 4th Monomer to Control Adhesion, etc.

Acid-Labile Group

Solubility Switch but Decreases Transparency

Aqueous Solubility

Transparency

CF₂CF₂

CH₂CH

OCH₂C(CF₃)₂OH

O-R
Fluorination and Transparency

Absorbance at 157: 6.8  1.3  0.7
Absorbance Data
TFE / NB-F-OH / Acrylate Copolymers

Absorbance at 157 mn (µm⁻¹)

% TFE
TFE Copolymer Properties

- TFE + norbornene-F-OH + acid-labile switch (alkyl acrylate)
  - 40 - 50 mole % norbornene fluoroalcohol
  - 15 - 40 mole % TFE
- Absorbance 0.7 - 2.7 µm\(^{-1}\)
  - Mostly controlled by ester content
- Etch rate 1.2 - 1.4 X Apex E
- Tg = 130 to 160 °C
- Mn = 3,000 - 15,000
  - Readily controlled by initiator concentration and/or use of chain transfer agent
- Soluble in standard organic solvents (e.g. acetone, THF)
Monomer Synthesis

Polymer Synthesis

• Solution, free-radical polymerization
  – 40 - 60 °C and 200 - 400 psi

• TFE / norbornene dipolymer
  – Strong tendency for monomers to alternate
    • Typical for fluorocarbon / hydrocarbon olefin mixtures
  – Simple batch copolymerizations give 50 / 50 copolymer

• TFE / norbornene / acrylate terpolymers
  – Acrylate most reactive monomer
  – Carefully controlled semibatch process to obtain uniform polymers:
    • Precharge norbornene-rich mixture
    • Maintain constant TFE pressure
    • Feed initiator and acrylate-rich monomer mixture
### TFE / Norbornene / t-Butyl Acrylate Copolymers

<table>
<thead>
<tr>
<th>Monomer Comp.</th>
<th>Init. (mol %)</th>
<th>Conv. (%)</th>
<th>Mn</th>
<th>Polym. Comp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TFE NBE TBA</td>
<td></td>
<td></td>
<td></td>
<td>TFE NBE TBA</td>
</tr>
<tr>
<td>70 30</td>
<td>0.25</td>
<td>31</td>
<td>6700</td>
<td>52 48</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>89</td>
<td>4900</td>
<td>70 30</td>
</tr>
<tr>
<td>68 30</td>
<td>0.25</td>
<td>26</td>
<td>5200</td>
<td>49 43 8</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>91</td>
<td>4500</td>
<td>64 32 4</td>
</tr>
<tr>
<td>65 30</td>
<td>0.25</td>
<td>24</td>
<td>6200</td>
<td>37 44 19</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>89</td>
<td>4300</td>
<td>56 40 5</td>
</tr>
<tr>
<td>60 30</td>
<td>0.25</td>
<td>27</td>
<td>6300</td>
<td>28 35 37</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>87</td>
<td>5600</td>
<td>53 35 13</td>
</tr>
<tr>
<td>50 30</td>
<td>0.25</td>
<td>29</td>
<td>9900</td>
<td>16 28 56</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>63</td>
<td>6400</td>
<td>42 40 18</td>
</tr>
</tbody>
</table>
Polymerization Issues

- TFE
  - Deflagrating Explosive & Cancer Suspect Agent
- Provisions for multiple monomer and initiator feeds throughout polymerization
  - Maintain product uniformity
- Meet customer needs for product quantity
  - Multiple reactors for production of 50 g to 5 Kg batches
- High purity
  - < 20 ppb each of multiple metals
    - Materials of construction
    - Monomer and solvent purity
    - Purification train
5 kg System Polymerizer

5 kg System Isolation

5 kg System Filtration/IX
TFE Tetrapolymer Imaging

80 nm 1:1.5 Lines
150 nm film thickness

AR19 BARC
PEB = 120°C
TFE Terpolymer

June 2002

Polymer absorption = 1.27 µm⁻¹

Absorption of formulated sample = 1.62 µm⁻¹
Contrast Curve DXR033L

Normalized Thickness vs Dose (mJ/cm²)

120 PEB
130 PEB
Etch Data

TFE Copolymers

Rate relative Apex-E

Poly etch

Oxide etch
Extensions and Future Directions

• Improved properties by incorporating more fluorine in polycyclic segment?
  – Needs to be remote from double bond for good polymerizability
• Bicyclo[2.2.1]heptene (NB) $\rightarrow$ Tricyclo[4.2.1.0^{2,5}]nonene (TCN)
## TFE / TCN Copolymers

<table>
<thead>
<tr>
<th>TFE Copolymer Properties</th>
<th>Tg</th>
<th>Absorbance at 157 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>150 °C</td>
<td>1.30</td>
</tr>
<tr>
<td></td>
<td>228 °C</td>
<td>0.69</td>
</tr>
<tr>
<td></td>
<td>213 °C</td>
<td>0.55</td>
</tr>
<tr>
<td></td>
<td>203 °C</td>
<td>0.61</td>
</tr>
</tbody>
</table>
TFE / Vinyl Ether Copolymers

- TFE Copolymerizes Readily with Vinyl Esters and Vinyl Ethers to Give Amorphous Copolymers:
  - TFE / Vinyl Acetate \( T_g = 48 \, ^\circ C \)
  - TFE / Butyl Vinyl Ether \( T_g = 20 \, ^\circ C \)
- \( T_g \) Too Low; Poor Etch Resistance for Resists
- Incorporate Pendant Groups
  - Bulky for High \( T_g \)
  - Carbon Rich (Polycyclic) for Etch Resistance
  - Saturated for Transparency
# TFE Copolymers

\[
\text{CF}_2\text{CF}_2 + \text{CH}_2=\text{CH} \rightarrow \text{CF}_2\text{CF}_2\text{CH}_2\text{CH}
\]

<table>
<thead>
<tr>
<th>R</th>
<th>Tg</th>
<th>Mn</th>
<th>Etch Rate</th>
<th>Absorbance at 157 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="R1" /></td>
<td>149 °C</td>
<td>33500</td>
<td>6.5</td>
<td>6.5</td>
</tr>
<tr>
<td><img src="image" alt="R2" /></td>
<td>86 °C</td>
<td>42800</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="R3" /></td>
<td>121 °C</td>
<td>37300</td>
<td>0.9</td>
<td>6.1</td>
</tr>
<tr>
<td><img src="image" alt="R4" /></td>
<td>140 °C</td>
<td>27500</td>
<td></td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="R5" /></td>
<td>66 °C</td>
<td>57400</td>
<td>1.0</td>
<td>3.3</td>
</tr>
</tbody>
</table>
TFE/Vinyl Ester and Vinyl Ether Copolymers

- Readily prepared in moderate to good conversion
- Significant Tg increase from adding bulky side chains
- Good etch resistance
- High absorbance at 157 nm

Saturation and Fluorination does not guarantee transparency at 157 nm

A. E. Feiring, E. R. Wonchoba, B. E. Fischel, T. V. Thieu, M. Reza Nassirpour
Hexafluoroisopropanol Groups in Polymers

- Excellent Hydrogen Bond Donor
- Less Tendency towards Self-Association than Phenols, Carboxylic Acids, Aliphatic Hydroxyls

\[ \text{Useful Substituent for Enhancing Polymer Miscibility} \]
Hexafluoroisopropanol Groups in Polymers

\[
\begin{align*}
\text{TFE-} & \text{alt-HFIPVE} \\
\text{CH}_2=\text{CHOCH}_2\text{CH}_2\text{OH} + & \begin{array}{c}
\text{O} \\
\text{CF}_3
\end{array}
& \rightarrow \\
\text{CH}_2=\text{CHOCH}_2\text{CH}_2\text{OCH}_2\text{COH} & \begin{array}{c}
\text{CF}_3 \\
\text{CF}_3
\end{array}
\end{align*}
\]

- Alternating 1:1 Copolymer
- \(\text{Mn} = 173000, \text{Mw} = 329000\)
- \(\text{Tg} = 12 \, ^\circ\text{C}\)
Polymer Blends with TFE-\textit{alt}-HFIPVE

- Polymer Miscibility Evaluated by Infrared and DSC
  - Polymethyl Methacrylate Miscible
  - Polyethyl Methacrylate Miscible
  - Polybutyl Methacrylate Miscible
  - Ethylene-co-Vinyl acetate (70 \%) Miscible
  - Polymethylvinyl Ether Miscible
  - Polyethylvinyl Ether Miscible
  - Polypropylvinyl ether Phase Separated
  - Polybutylvinyl Ether Phase Separated

- HFIP Group is powerful blending agent but very sensitive to steric effects

Infrared Studies of Blends with Polyethers

TFE- $alt$ -HFIPVE/Polyether Blends
1:4 Molar
DSC Data on Blends

![Graph showing DSC data on blends]
Summary

• Fluorinated groups critical for transparency and development in next generation photoresists

• Demonstrated:
  – Fluoropolymers with good transparency, etch resistance, thermal stability and aqueous developability
  – 60 nm isolated line imaging of ~160 nm thick resists
  – Manufacture on multikilogram scale

• Families of novel amorphous, high Tg TFE copolymers
  – TFE / TCN Copolymers
  – TFE / Bulky vinyl esters and vinyl ethers

• Utility of hexafluoroisopropanol groups in polymers

• Continuing challenge for resists: Optimize properties in a single polymer
The Resist Teams

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Jerry Feldman, Mary Blasko
Slava Petrov, Bob Smith
Bob Wheland, Gregg McCauley
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Corporate Center for Analytical Science

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