Resist Technology for the Post-157nm Lithography Era: Issues and Perspectives

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Outline

• Introduction
  • Post-157nm lithography options
  • Resist technology options for post-157nm lithography
    • Conventional resist technology approaches
    • Emerging resist technology approaches
  • Post-157nm lithography resist technology issues
    • Conventional resist technology issues
      • Limitations of chemical amplification reaction system in resists
        • Uncontrollable diffusion
        • Image spread and image blur
  • Ultrathin film imaging issues
    • Film instability & defects
    • Film thermophysical property changes
      • Enhanced acid transport
      • Enhanced sensitivity to contamination
      • Enhanced deprotection kinetics
Outline cont’d

• Emerging resist technologies
• Environmental health and safety concerns
• Integrating conventional and emerging resist technologies
• Concluding remarks
Post-157nm Lithography Technologies

EUVL

\[ \text{hv} \quad (\lambda=13.5 \text{ nm}) \]

Resist coated wafers

EPL

\[ \text{e}^- \quad @ 100KV \]
Resist technology approaches for Post-157nm Lithography

- Conventional techniques
  - Single Layer (SL) scheme
  - Thin Imaging Layer/Hardmask Scheme (TLI/HM)
  - Surface Silylation Scheme (SSS)

- Emerging techniques
  - Nanoimprinting Techniques “Soft Lithography”
  - Self-Assembly
Conventional resist technology approaches for post-157nm lithography – issues & prospects

<table>
<thead>
<tr>
<th>Issue</th>
<th>SL</th>
<th>TLI/HM</th>
<th>SSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transparency</td>
<td>Too opaque at nominal thickness</td>
<td>Good</td>
<td>Opacity is an advantage</td>
</tr>
<tr>
<td>Etch Resistance</td>
<td>Insufficient</td>
<td>Excellent Etch selectivity issues</td>
<td>Good (Thin SiOx good etch mask) Etch &amp; silylation selectivity issues</td>
</tr>
<tr>
<td>Process</td>
<td>Simple</td>
<td>Imaging &amp; processing separated (a plus)</td>
<td>Complex processing (Feature dependent silylation)</td>
</tr>
<tr>
<td>Process control</td>
<td>Not an issue</td>
<td>Not an issue</td>
<td>A serious issue</td>
</tr>
</tbody>
</table>
### Conventional resist technology approaches for post-157nm lithography – issues & prospects

<table>
<thead>
<tr>
<th>Issue</th>
<th>SL</th>
<th>TLI/HM</th>
<th>SSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>LER</td>
<td>An issue</td>
<td>Problem</td>
<td>&gt;10 nm</td>
</tr>
<tr>
<td>Resolution</td>
<td>Poor</td>
<td>High</td>
<td>Moderate</td>
</tr>
<tr>
<td>Sensitivity</td>
<td>Low (CA)</td>
<td>Low (CA)</td>
<td>Very low (CA)</td>
</tr>
<tr>
<td>Diffusion</td>
<td>Stability CD control issues</td>
<td>Problem</td>
<td>A serious problem</td>
</tr>
<tr>
<td>Defects</td>
<td>An issue</td>
<td>Not a serious issue</td>
<td>A serious problem</td>
</tr>
</tbody>
</table>
Resist outgassing in vacuum

Sources of volatile organic materials include:
-- protecting groups (majority contributor)
-- photoacid generators
-- solvent hydrolysis
Most resists (and neat polymers) show both an exposure-induced mass increase (E<10 mJ/cm²) and mass loss (E>40 mJ/cm²)

<table>
<thead>
<tr>
<th>Resist</th>
<th>Mass liberated per year (g)</th>
<th>QCM Results (molecules/cm²-sec)</th>
<th>GCMS Results (molecules/cm²-sec)</th>
<th>Thickness deposited (nm) e=10⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>IBM V2.1</td>
<td>0.7</td>
<td>3x10¹²</td>
<td>2x10¹²</td>
<td>70</td>
</tr>
<tr>
<td>Shipley XP-7022</td>
<td>1</td>
<td>4x10¹²</td>
<td>3x10¹²</td>
<td>100</td>
</tr>
<tr>
<td>OMM RX-1</td>
<td>0.3</td>
<td>&lt;1x10¹²</td>
<td>1x10¹²</td>
<td>30</td>
</tr>
<tr>
<td>OMM bilayer</td>
<td>18</td>
<td>4x10¹³</td>
<td></td>
<td>1800</td>
</tr>
<tr>
<td>Sumitomo NEK-304</td>
<td>&lt;0.3</td>
<td>&lt;1x10¹²</td>
<td></td>
<td>&lt;30</td>
</tr>
</tbody>
</table>

Source: Kunz, R. *Personal Communications*, MIT Lincoln Labs, 1998
<table>
<thead>
<tr>
<th>Resist Parameter</th>
<th>EPL</th>
<th>EUVL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Image distortion due to nonconducting resist film</td>
<td>A possibility</td>
<td>Not a problem</td>
</tr>
<tr>
<td>Outgassing</td>
<td>A problem</td>
<td>A problem</td>
</tr>
<tr>
<td>(key to preventing charging effects due to contamination build-up in column)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Substrate &amp; resist heating</td>
<td>A problem</td>
<td>Not a problem</td>
</tr>
<tr>
<td>Contrast requirement</td>
<td>&gt;5</td>
<td>Has to be high</td>
</tr>
<tr>
<td></td>
<td>High contrast compensates for the backscattered $e^-$ that reduces the image contrast</td>
<td>to improve LER</td>
</tr>
</tbody>
</table>
## Summary of issues with conventional resist technology in post-157nm lithography

<table>
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<tr>
<th>Resist Parameter</th>
<th>EPL</th>
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</thead>
<tbody>
<tr>
<td>Tg</td>
<td>&gt; max. temp rise due to e-beam heating, so as to prevent unwanted diffusion in the resist &amp; loss of pattern fidelity</td>
<td>High enough to prevent dark reactions</td>
</tr>
<tr>
<td>Resolution loss due to Uncontrollable diffusion</td>
<td>A problem</td>
<td>A problem</td>
</tr>
<tr>
<td>Line edge roughness</td>
<td>A problem</td>
<td>A problem</td>
</tr>
<tr>
<td>Charging</td>
<td>A problem</td>
<td>Not a problem</td>
</tr>
<tr>
<td>Shot noise limit</td>
<td>A problem</td>
<td>A problem</td>
</tr>
<tr>
<td>Pattern collapse</td>
<td>A problem</td>
<td>A problem</td>
</tr>
</tbody>
</table>
Emerging resist technology options for post-157nm lithography

- Nano-imprint techniques “soft lithography”
- Self-assembly techniques
- Direct patterning techniques
Principle of chemical amplification

- Chemical amplification allows a single photoproduct to cause many solubility-switching reactions.
Achilles heel of chemical amplification resist system: uncontrolled acid diffusion

Exposure

Post Exposure Bake

Develop

12/12/02   NSF-SRC ERC Presentation
Calculated effect of diffusion on blurring

**Effect of Diffusion**

The initial acid concentration $[H^+]$ is defined by the aerial image.

Fig. 1. Measured diffusional length ($d_{dev}$) of perfluorooctanesulfonic acid (PFOS) in PBOCST at different temperatures: ($\times$) 90 °C, ($\Delta$) 100 °C, (+) 110 °C, (□) 120 °C, (■) 130 °C. Thickness: 1250 Å. The standard uncertainty in the $d_{dev}$ measurement is ±10 Å.

Fig. 2. Diffusion of PFOS into PBOCST at different temperatures. ($\times$) 90 °C, ($\Delta$) 100 °C, (+) 110 °C, (□) 120 °C, (■) 130 °C. Thickness: 1250 Å. The standard uncertainty in the $d_{dev}$ measurement is ±10 Å.

Diffusion coefficient as a function of film thickness

Profile shows asymptotic behavior at ~600Å, below which diffusion slows down remarkably, probably due to interfacial effects.

$D_{\text{eff}}$ as a function of film thickness for PFOS in PBOCST at 110 °C.

Humidity Effects on Deprotection Kinetics

kinetics when the resist (TBOC) is purged with various gases (80°C PEB)

Leveling effect of water -- implications for exposures in vacuum

Nitrogen:

Dry Air

Nitrogen bubbled through H₂O:

Sean Burns, UT-Austin (2002) – private communication
The Effect of Humidity on TBOC/PHOST Copolymer Deprotection Kinetics

Leveling effect of water -- implications for exposures in vacuum
Sean Burns, UT-Austin (2002) – private communication
Effect of humidity on low activation energy resists

KRS-XE

• used primarily for e-beam photomask writing
• Insensitive to post exposure delays (reaction goes at room temp.)
• Insensitive to minor temperature fluctuations
• Requires water in order for deprotection to occur

Sean Burns, UT-Austin (2002) – private communication
Kinetics of KRS-XE deprotection under various % RH

Leveling effect of water -- implications for exposures in vacuum

Sean Burns, UT-Austin (2002) – private communication
Effect of Humidity on Deprotection Kinetics of UV6

Implications for exposures in vacuum

Sean Burns, UT-Austin (2002) – private communication
Final Acid Diffusion Distance vs. % RH

Leveling effect of water -- implications for exposures in vacuum

Sean Burns, UT-Austin (2002) – private communication
Film thermophysical property changes with thickness

Thermal Probe Measurements of Tg in UTF

- Bulk Film
- Localization effects
- Substrate effects

Bulk $T_g$ of PMMA (100.3 kg/mol)

UTR film issue: thin film stability dispersion curve of polystyrene film

\[ (A = 8 \times 10^{-20} \text{ J}, \ \gamma = 40 \times 10^{-3} \text{ J/m}^2) \]

\[ s = \frac{q^2}{\eta} \left[ -\gamma q^2 h_o^3 + \frac{A}{2 \pi h_o} \right] \]

\[ \tau_{\text{min}} = \frac{4^2 \pi^2 \eta h_o^5 \gamma}{A^2} \]

\[ q_c = \frac{1}{h_o^2} \sqrt{\frac{A}{2 \pi \gamma}} \]

Critical wave\# increases like \( 1/h_o^2 \) as the film thickness \( h_o \) decreases

\( q < q_c, (A/2 \pi h_o > \gamma q^2 h_o^3), \ \tau \) is positive and surface disturbances are amplified exponentially, eventually reaching the substrate and nucleating a hole.

If \( \tau_{\text{min}} << \) time required for resist spinning, drying and curing, then disturbances will continue to grow exponentially and will eventually rupture the film before it has a chance to solidify.


Ultrathin film imaging issue: thin film instabilities

Films layer density and roughness as a function of Shipley XP-98248 (phenolic ESCAP polymer based resist) of thickness. Film was spincoated on Si wafer. X-ray reflectivity measurements.

Onset of film instability \( \sim \) <53nm

Ultrathin film imaging issue: Tg depression with film thickness

Fox Equation

\[
\frac{1}{T_g} = \frac{M_1}{T_{g1}} + \frac{M_2}{T_{g2}}
\]

Depression of Tg with Film thickness.

Ultrathin film imaging issue: enhanced environmental sensitivity of UTR films

180nm 1:1.5 Features
SEM images of line and space patterns printed with ~60 nm thick Shipley XP-98248 (phenolic ESCAP polymer based) resist on bare silicon and exposed at 157-nm.

130nm 1:2 Features

Emerging resist technology options for post-157nm lithography: nano-imprinting

1. Imprint
   - Press Mold
   - Mold
   - Resist
   - Substrate

   10nm resolution achieved
   Process is fast
   Reduces the amount of chemicals

2. Pattern Transfer
   - RIE

   Issues: flat substrate, defects (particles, poor adhesion, bubbles), 1x printing and mask defect issues

Patterning is by deforming the coated polymer (polydimethylsiloxane) shape through embossing (with a mold), rather than by altering resist through radiation (with particle beams). Following imprinting, anisotropic etch is used to remove resist residues in the compressed area to expose the underneath substrate.

Emerging resist technology options for post-157nm lithography: Direct patterning technique (Laser-Assisted Direct Imprint (LADI))

XeCl “excimer” laser with 20ns pulse, a transparent patterned quartz mold to mechanically imprint the molten surface of a silicon wafer. Surface quickly solidifies and, because there is no adhesion between the quartz and silicon, the mold can be removed without damage.

- Extremely high resolution
- Process is fast
- No chemicals!
- No pattern collapse issue

Issues: flat substrate
1x printing and mask defect issues

Emerging resist technology options for post-157nm lithography: Lithographically Induced Self-Assembly (LISA)

Mask is held apart from the polymer surface by spacers. The system is heated above the Tg of the polymer, such that the polymer rises up against the forces of gravity and surface Tension, forming periodic structures that are aligned to any pattern on the mask.

LADI results

Imprint mold with 10nm diameter pillars

10nm diameter holes imprinted in PMMA

10nm diameter metal dots fabricated by NIL

Summary

• Conventional resist technology will be resolution limited at post-157nm lithography era design rules
  • Chemical amplification chemistry runs into “diffusional limits”
  • Thin film instabilities and degradation of thermophysical properties will become significant.

• Nanoimprinting and self-assembly techniques appear promising, but challenges remain.
  • High resolution with high throughput potential
  • Environmentally friendly
  • Defects remain a concern

• Integrating the best attributes of conventional lithography with those of emerging techniques are feasible and appear promising.
  • Laser-assisted direct imprint & lithographically-induced self assembly are steps in the right direction
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