Review* of Metallic Resists for EUV

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I. Metal-Oxo Films (OSU/Inpria)
II. HfO\textsubscript{x} and ZrO\textsubscript{x} Nanoparticles (Cornell)
III. Molecular Organometallic Resists for EUV (MORE)
\quad (SUNY Poly and New Paltz)
\quad A. Tin Oxo Clusters (Cardineau)
\quad B. Tin Carboxylates (Del Re)
\quad C. Transition Metal Oxalates (Freedman)
\quad D. Positive-Tone Palladium (Sortland)
\quad E. High-Speed Main-Group Olefins (Passarelli)

IV. Acknowledgements

*For 2\textsuperscript{nd} Edition:
Optical Density Map of the Elements

EUV OD at Std. State Density (Relative to Carbon)
0-2 2-4 4-6 6-8 8-10 10-12

Inpria HafSOx
Super-Fast Nanoparticles
Negative Tone

Inpria SnOx
Positive Tone

Tin-Oxo Cluster
Super-Low LER

HfO₂

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SUNY Polytechnic Institute
I. Metal-Oxo Films (OSU/Inpria)

First Publication of EUV Results. BMET SPIE 2010
I. Metal-Oxo Films (OSU/Inpria) Published Photoreactivity

The key to the photoreactivity of the HafSOx resists appears to be controlling the dehydration reaction (eq 1) which crosslinks and thereby reduces the solubility of these metal oxo-films. Dehydration is prevented by binding peroxide to Hf. Fortunately, the metal peroxide decomposition can be induced by high-energy light or electrons (eq 2) thereby creating metal hydroxides that can condense and become insoluble.

In brief, the metal peroxides allow the resists to dissolve in the unexposed regions and upon photolysis the metal peroxides become metal hydroxides and condense to become insoluble features of the negative-tone resists.

\[
\text{Hf} - \text{OH} + \text{HO} - \text{Hf} \quad \rightarrow \quad \text{Hf} - \text{O} - \text{Hf} + \text{H}_2\text{O}
\]
(1)

\[
\text{Hf}_2\text{O}_2 + \text{O}_2\text{Hf} \quad \xrightarrow{\text{hv}, \text{e}^-} \quad \text{Hf}_2\text{O}_2\text{H} + \text{H}_2\text{O}_2\text{Hf}
\]
(2)
I. Metal-Oxo Films (OSU/Inpria) 
Imaging at PSI (2014)
I. Metal-Oxo Films (OSU/Inpria)
Imaging at PSI (2014)

HP=12 nm

HP=8 nm
II. HfO$_x$ and ZrO$_x$ Nanoparticles (Cornell)

Many versions of these resists were prepared using methacrylate as a ligand and formulated with either photoacid generators or free-radical initiators, suggesting that the negative-tone imaging mechanisms might involve free-radical crosslinking.

However, careful studies revealed that the negative-tone solubility switches do not involve free-radical crosslinking, but instead involves a ligand exchange mechanism that can proceed without PAGs or with the assistance of PAGs.

Size distribution of nanoparticle suspensions
II. HfOx and ZrOx Nanoparticles (Cornell)

These nanoparticle resists are capable of good EUV patterning capability at extremely fast photospeeds. 20 and 30 nm isolated lines were printed using doses of 2.4 and 1.6 mJ/cm².

Although the LER values of these resists are modest (5-7 nm), the LER is not too poor considering that the resists are extremely sensitive and are composed of nanoparticles that are 1-2 nm in diameter.
III. MORE: A. Tin Oxo Clusters (Cardineau)

\[(\text{PhSn})_{12}\text{O}_{14}(\text{OH})_{6}]\text{Cl}_2\]

Dose: 350 mJ/cm\(^2\)
Resolution: 18 nm

The resist sensitivity shows good correlation with anion size.
<table>
<thead>
<tr>
<th>LER (nm)</th>
<th>Dose (mJ/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.9</td>
<td>560</td>
</tr>
<tr>
<td>3.0</td>
<td>560</td>
</tr>
<tr>
<td>3.9</td>
<td>560</td>
</tr>
<tr>
<td>7.3</td>
<td>560</td>
</tr>
<tr>
<td>9.4</td>
<td>560</td>
</tr>
<tr>
<td>4.5</td>
<td>520</td>
</tr>
<tr>
<td>2.5</td>
<td>520</td>
</tr>
<tr>
<td>3.6</td>
<td>520</td>
</tr>
<tr>
<td>9.0</td>
<td>520</td>
</tr>
<tr>
<td>6.2</td>
<td>520</td>
</tr>
<tr>
<td>2.9</td>
<td>380</td>
</tr>
<tr>
<td>3.8</td>
<td>380</td>
</tr>
<tr>
<td>3.8</td>
<td>380</td>
</tr>
<tr>
<td>7.6</td>
<td>380</td>
</tr>
<tr>
<td>7.7</td>
<td>380</td>
</tr>
<tr>
<td>8.1</td>
<td>380</td>
</tr>
<tr>
<td>8.9</td>
<td>350</td>
</tr>
<tr>
<td>5.5</td>
<td>760</td>
</tr>
<tr>
<td>5.5</td>
<td>350</td>
</tr>
<tr>
<td>14</td>
<td>700</td>
</tr>
<tr>
<td>14</td>
<td>320</td>
</tr>
<tr>
<td>13</td>
<td>350</td>
</tr>
</tbody>
</table>

Resolution Capabilities for Various Anions.

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II. MORE: B. Low LER Tin Resists (Del Re)

![Chemical structures](attachment:chemical_structures.png)

<table>
<thead>
<tr>
<th>Dose (mJ/cm²)</th>
<th>LER (nm)</th>
<th>LWR (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>13</td>
<td>8.9</td>
</tr>
<tr>
<td>300</td>
<td>1.9</td>
<td>1.6</td>
</tr>
<tr>
<td>360</td>
<td>2.9</td>
<td>1.9</td>
</tr>
<tr>
<td>600</td>
<td>1.7</td>
<td>1.2</td>
</tr>
<tr>
<td>43</td>
<td>8.9</td>
<td>8.1</td>
</tr>
<tr>
<td>300</td>
<td>1.9</td>
<td>1.4</td>
</tr>
<tr>
<td>410</td>
<td>3.2</td>
<td>2.2</td>
</tr>
<tr>
<td>600</td>
<td>1.7</td>
<td>1.1</td>
</tr>
</tbody>
</table>

- **50 nm**
- **35 nm**

2000 RPM

4000 RPM
II. MORE:  B. Low LER Tin Resists (Del Re)
LER Does Not Follow Z Parameter

Theoretical LWR and LER

Measured LWR and LER

CD: 35 nm
LER: 1.4 nm
LWR: 1.9 nm

LWR and LER

Dose = 300 mJ/cm²
III. MORE: C. Transition Metal Oxalates (Freedman)

\[ \text{PBzPh}_3^+ \text{Co} \text{O}_2 \text{O} \rightarrow \text{PBzPh}_3^+ \text{Co} \text{O}_2 \text{O} + 2\text{CO}_2 + 2\text{e}^- \]

18 nm
30 mJ/cm²
III. MORE: C. Transition Metal Oxalates (Freedman)

Central Metal (M):

<table>
<thead>
<tr>
<th>Cr</th>
<th>Fe</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>35 nm h/p lines:</td>
<td>![Cr image]</td>
<td>![Fe image]</td>
</tr>
<tr>
<td>$E_{\text{size}}$ (mJ/cm$^2$):</td>
<td>70</td>
<td>48</td>
</tr>
</tbody>
</table>
III. MORE: D. Positive-Tone Palladium Resists (Sortland)

\[ \text{L-Pd-L} + 4 \text{CO}_2 + \text{Pd}_{(m)} \]

\[
\begin{align*}
21 & \quad \text{Ph}_2\text{P} & \quad \text{Ph}_2\text{O} & \quad \text{O} & \quad \text{O} \\
22 & \quad \text{Ph}_2\text{P} & \quad \text{Pd} & \quad \text{Ph}_2\text{O} & \quad \text{O} & \quad \text{O} \\
23 & \quad \text{Ph}_2\text{P} & \quad \text{Pd} & \quad \text{Ph}_2\text{O} & \quad \text{O} & \quad \text{O} \\
24 & \quad \text{Et}_3\text{P} & \quad \text{Pt} & \quad \text{O} & \quad \text{O} \\
25 & \quad \text{Et}_3\text{P} & \quad \text{Pd} & \quad \text{O} & \quad \text{O} \\
26 & \quad \text{MePh}_2\text{P} & \quad \text{Pd} & \quad \text{O} & \quad \text{O} \\
27 & \quad \text{EtPh}_2\text{P} & \quad \text{Pd} & \quad \text{O} & \quad \text{O}
\end{align*}
\]

- 247 mJ/cm²
- 54 mJ/cm²
- 157 mJ/cm²
- 110 mJ/cm²

\( E_{size} = 50 \text{ mJ/cm}^2 \)
III. MORE: E. High-Speed Main-Group Olefins (Passarelli)

Excellent sensitivity at modest resolution.

![JP-20:](image)

Dose = 5.6 mJ/cm²

50 nm | 35 nm | 25 nm

**Proposed mechanism is based on photo-initiated free radical polymerization.**

**Initiation:**

\[

\text{JP-20} \xrightarrow{\text{hv or e-}} \text{Polymerizable Olefin}
\]

**Propagation:**

\[

R = \text{metal or carboxylate centered radicals}
\]

Exposed region crosslinked: less soluble in developer

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EUV Symposium 6/16
Brainard and Brainard
Passarelli & Brainard JM3 2015 043503
III. MORE:  E. High-Speed Main-Group Olefins (Passarelli)

\[ M = \text{Sb, Bi, Sn or Te} \]
\[ R = \text{Aliphatic or Aromatic Sb - C Group} \]
\[ O_2CR' = \text{Carboxylate Group} \]

JP-20: 

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{Sb} & \quad \text{Sb} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

\[
\begin{align*}
\text{R'} & \quad \text{R} \\
\text{O} & \quad \text{O} \\
\text{M} & \quad \text{R} \\
\end{align*}
\]

Dose (mJ/cm²) 

JP-20: 5.6 

JP-30: 14, 14 

MM-3: 56 

50 nm 

14 

40 nm 

14 

30 nm 

14 

30 nm
III. MORE: E. High-Speed Main-Group Olefins (Passarelli)

Unexpected Result: Changing Sb-R bond did not dramatically affect sensitivity.

**Sensitivity Hypothesis:** The ratio of polymerizable olefins to space filling R groups is the largest contributor to sensitivity characteristics of antimony acrylate resists.

\[ \text{POL} = \frac{\# \text{ of Polymerizable Olefins}}{\# \text{ of Atoms (Excluding Hydrogen)}} \times 100\% \]
III. MORE: E. High-Speed Main-Group Olefins (Passarelli)
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