Aqueous Materials for Advanced Lithography

Strategic Materials Conference Taiwan 2019

Yi Cao
Taipei, 9/19/2019
agenda

01 Overview and product roadmap
02 Rinse materials
03 Chemical shrink materials
04 Summary
01 overview and product roadmap
Merck Performance Materials – Semiconductor Solutions

Our solutions enable electronic industry

- smaller structures to continue Moore’s law
- higher memory capacity, faster processing speed and less power consumption
- improved yields and lower processing costs

Further expanded portfolio with the on-going Versum acquisition
✓ EUV process makes economic sense when replacing 3 masks.
✓ Double SAQP for pillar patterning may render EUV process of cost advantages.
# Lithography & cleaning materials roadmap

<table>
<thead>
<tr>
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<th>15</th>
<th>16</th>
<th>17</th>
<th>18</th>
<th>19</th>
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<tr>
<td>Logic</td>
<td>14nm</td>
<td>10nm</td>
<td>7nm</td>
<td>5nm</td>
<td>3nm?</td>
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<td>DRAM</td>
<td>20nm</td>
<td>1X</td>
<td>1Y</td>
<td>1Z</td>
<td>1? &amp; beyond</td>
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<td>2D NAND</td>
<td>15/16nm</td>
<td>14nm</td>
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<tr>
<td>3D NAND</td>
<td>32/36L</td>
<td>48L</td>
<td>64/72L</td>
<td>92/96L</td>
<td>128L</td>
<td>256L &amp; beyond</td>
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**Patterning**
- TARC (i-line /KrF)
- OBARC (KrF/ArF/ArF-i)
- Generic SOC
- KrF/i-line Thick Film Resists

**Yield improvement**
- Rinse material (KrF/ArF/ArF-i)
- Rinse material (EUV)
- PTD Shrink Material (KrF/ArF)
- Novel rinse material

**Advanced cleaning**
- NTD Shrink Material
- Novel post-etch cleaning solutions

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<table>
<thead>
<tr>
<th><strong>Commercial product</strong></th>
<th><strong>Development stage</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal Hard Mask / EPL</td>
<td>DSA</td>
</tr>
<tr>
<td>Specialty SOC</td>
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</tbody>
</table>

**Rinse material (KrF/ArF/ArF-i)**

**OBARC (KrF/ArF/ArF-i)**

**TARC (i-line /KrF)**

**Specialty SOC**

**DSA**

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Aqueous materials for advanced lithography | Strategic Materials Conference Taiwan | Sep. 19, 2019
Rinse materials

Concept

Pattern collapse:
- Capillary effect (rinse surface tension)
- Resist deformation (Young’s modulus)

Defect reduction & LWR, LER improvement:
- Resist & DIW affinity part of FIRM chemical
- Clean resist scum & leveling pattern surface

\[ \sigma_{\text{max}} = 6\gamma A^2 \cdot \cos \theta / D \]

- \( \sigma \) : Stress to resist
- \( \gamma \) : Surface tension of rinse
- \( A \) : Aspect ratio = H/W
- \( \Theta \) : Contact angle
- \( D \) : Space width
Rinse materials

The process and benefits

Fully integrated in resist development
Rinse materials

The process and benefits

**Key Benefits**

- Straightforward process
- Pattern collapse mitigation
- Defect reduction
Rinse materials

Material design

*Affinity between resist and surfactant
(Penetration of surfactant into resist pattern)

Considerations

- Resist chemistry
- Loading of surfactants
- Bulkiness of surfactants
- Melting control
- Functionality

Surfactant penetration is one of the key factors for resist compatibility

*The affinity is defined by solubility parameter.
Rinse materials – ArF
Commercial products

<table>
<thead>
<tr>
<th>Product Name</th>
<th>SPC-116A</th>
<th>SPC-124A</th>
<th>SPC-402</th>
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<tr>
<td>*Surface tension (mN/m)</td>
<td>33.3</td>
<td>37.5</td>
<td>33.4</td>
</tr>
<tr>
<td>Chemical</td>
<td>Nonionic</td>
<td>Nonionic</td>
<td>Nonionic + Additive</td>
</tr>
<tr>
<td>Application</td>
<td>ArF-d</td>
<td>KrF &amp; ArF-d (ArF-i)</td>
<td>ArF-i</td>
</tr>
</tbody>
</table>

Introduction of melting inhibitor

- Broadly adopted in the industry.
- Proven resist compatibility.
Rinse materials

EUV Rinse – development roadmap

- Gen. 1: Extreme 1x
  - SPC-6xx
  - Improved process margin & PR compatibility

- Gen. 2: Gen. 2
  - SPC-7xx
  - Pattern collapse
  - Nanobridges

- Gen. 3: Gen. 3
  - SPC-75x

Customized formulations for new EUV resists

Prototype

2010 2013 2016 2019
Rinse materials
Lithographic performance on EUV Resist B

**Process conditions**

Exposure tool: NXE3300 (0.33NA, Dipole)
EUV Resist B/ 45nm thick (**16nm L/S**)
Dose: 41 mJ/cm² center / 1.5mJ/cm² step
Focus: 0.02um center / 0.02um step

<table>
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<tr>
<th></th>
<th>DIW</th>
<th>Gen. 2</th>
<th>Gen. 3</th>
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<tr>
<td>Minimum CD (nm)</td>
<td>N/A</td>
<td>15.5</td>
<td>14.5</td>
</tr>
<tr>
<td>(Pattern collapse margin)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Expanded process margin with new rinse platforms.
Rinse materials

Lithographic performance on EUV Resist C

**Process conditions**

**Exposure tool:** NXE3300 (0.33NA, Dipole)

EUV Resist C / 35nm thick (16/nm hp)

**Dose:** 53 mJ/cm² center / 2.0mJ/cm² step

**Focus:** 0.04µm center / 0.02µm step

**Gen. 2**

- Process window is improved by both material design and process optimization.
- 65 blocks

**Gen. 3**

- 71 blocks

**Gen. 3 & process optimization**

- 73 blocks

**Process window is improved by both material design and process optimization.**
Rinse materials
EUV rinse – defectivity

Process conditions
Exposure tool: NXE3300 (0.33NA, Dipole)
EUV resist / 35nm thick (18nm L/S)
Dose / Focus: 40.5 mJ/cm² / -0.05µm
Inspection area (Exposed area): 161.2cm²

- Pattern collapse dominates in regular process.
- Rinse process is effective in eliminating defects.
- Pinching defects are reduced with rinse process.
• **Rinse materials** offer benefits of pattern collapse mitigation and defect improvement, therefore, superior process margins for yield improvement.

• Merck offers rinse materials for both ArF and EUV lithography processes.

• Rinse process has been implemented in volume production of the first generation of EUV lithography.

• 16nm half pitch is resolved with rinse process with sufficient pattern collapse margin.

• Defectivity is significantly improved with EUV rinse.

• Collaborating with TEL, Merck offers not only innovative materials but also expertise in process optimization.
Chemical shrink materials
Shrink materials
The process & mechanism

- **ADI**
  - Substrate

- **SHM**
  - Substrate

- **MB**
  - Substrate

- **DIW dev.**
  - Substrate

**Schematic image**
- **Resist**
- **SHM**
- **Mixing layer**
- **Insoluble in DIW**
- **Shrinkage**

**ADDITIONAL NOTES**
- Constant shrinkage through pitch
- Whole track compatible process
- In-process tunable shrinkage
- Reduced Cost of Ownership
Shrink materials

Shrinkage controllability

**Shrink Process**
- **Film thickness:** 100nm
- **Mixing Bake:** 110, 130, 150°C/60sec
- **Development:** DI-Water

**Shrink amount is tunable with mixing bake temperature.**

<table>
<thead>
<tr>
<th>Mix bake temperature (°C)</th>
<th>Top Image</th>
<th>ADI</th>
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<tr>
<td></td>
<td><img src="image1" alt="Top Image" /></td>
<td><img src="image2" alt="Top Image" /></td>
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<tr>
<td>CD (nm)</td>
<td>55.0</td>
<td>65.5</td>
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<tr>
<td>Shrinkage (nm)</td>
<td>10.5</td>
<td><strong>11.3</strong></td>
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</table>
**Shrink materials**

**Local CD uniformity**

**Grid hole: 110nm pitch**

<table>
<thead>
<tr>
<th></th>
<th>Focus</th>
<th>-0.175 um</th>
<th>-0.150 um</th>
<th>-0.125 um</th>
<th>-0.100 um</th>
<th>-0.075 um</th>
<th>-0.050 um</th>
<th>-0.025 um</th>
<th>0.000 um</th>
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<tbody>
<tr>
<td>Control (ADI)</td>
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<tr>
<td>StDev CD</td>
<td>2.51</td>
<td>2.46</td>
<td>2.56</td>
<td>2.34</td>
<td>2.65</td>
<td>2.38</td>
<td>2.45</td>
<td>2.2</td>
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<tr>
<td>NSM-314 Shrink-D</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>StDev CD</td>
<td>1.05</td>
<td>1.24</td>
<td>1.41</td>
<td>1.31</td>
<td>1.33</td>
<td>1.18</td>
<td>1.27</td>
<td>1.05</td>
<td></td>
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<tr>
<td>Shrinkage</td>
<td>12.2 nm</td>
<td>13.2 nm</td>
<td>14.4 nm</td>
<td>14.6 nm</td>
<td>14.8 nm</td>
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<tr>
<td>NSM-530 Shrink-D</td>
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<tr>
<td>StDev CD</td>
<td>1.32</td>
<td>1.18</td>
<td>1.05</td>
<td>0.95</td>
<td>1.05</td>
<td>1.01</td>
<td>0.89</td>
<td>0.87</td>
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<tr>
<td>Shrinkage</td>
<td>16.4 nm</td>
<td>18.3 nm</td>
<td>19.4 nm</td>
<td>19.5 nm</td>
<td>19.8 nm</td>
<td>18.1 nm</td>
<td>17.9 nm</td>
<td>15.8 nm</td>
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Local CD Uniformity is improved by >50%.
Shrink materials
Proximity effects

Test Conditions
NTD resist
Shrink Materials: NSM-314, 530
Mixing Bake: 110, 130°C / 60sec
Development: DI-Water

Resist Pattern Pitch

*ID bias = Isolated and dense pattern bias

Significantly higher shrinkage and lower iso-dense bias are achieved with NSM-530.
Shrinkage (nm)

**Test conditions**
NTD resists from multiple suppliers
*Shrink*: 1st Gen shrink material and NSM-314
*Mixing Bake*: 150°C/60sec
*Development*: DIW

**Graph**

- **AX2110**: 20 nm
- **Resist A**: 18 nm
- **Resist B**: 15 nm
- **Resist C**: 14 nm

**Good compatibility with various resists.**
04 Summary
• Merck is specialized in aqueous materials to enhance photoresist performance.

• **Rinse process** has been proven effective in mitigating pattern collapse, improving process margin, and depressing defectivity in multiple generations of lithography.

• **Chemical shrink** is a viable technology assisting pattern scaling with:
  ✓ Cost-effective process enhancing resolution
  ✓ Improvement of DOF & local CD uniformity with shrinkage tunable by process
  ✓ Reduced proximity effects