EIDEC Outgas Testing Update

Soichi Inoue,
Toshiya Takahashi, Norihiko Sugie, Yukiko Kikuchi, Isamu Takagi,
Kazuhiro Katayama, Eishi Shiobara and Hiroyuki Tanaka

EUVL Infrastructure Development Center, Inc.
Outline

1. Current Status of Resist Outgas Qualification

2. Proposal on XPS Measurement Condition (Co-work with NIST & ASML)

3. Impact of Mask Open Ratio

4. Other Topics: papers in EUVL Symposium (Co-work with Univ. of Hyogo)

5. Summary
Co-workers

◆ Proposal on XPS Measurement Condition

*Shannon Hill and Thomas Lucatorto, NIST*
*Noreen Harned, ASML*

◆ Other Topics

(1) Resist Outgassing Characterization of PAG-Blended and PAG-Bound Systems (Oct. 10, 14:10 – 14:30)

(2) Study of the Relation Between Resist Components and Outgassing Contamination Species (Oct. 10, 14:30 – 14:50)

*Takeo Watanabe, Tetsuo Harada, and Hiroo Kinoshita, Center for EUVL, University of Hyogo*
Outline

1. Current Status of Resist Outgas Qualification

2. Proposal on XPS Measurement Condition (Co-work with NIST & ASML)

3. Impact of Mask Open Ratio

4. Other Topics: papers in EUVL Symposium (Co-work with Univ. of Hyogo)

5. Summary
Cleanable Contamination

As of Feb. 21, 2013

As of Oct. 1, 2013

• 77% of tested samples were met to cleanable contamination specification.
Accumulated Test Result for Commercial Resists (2)

Non-Cleanable Contamination

As of Feb. 21, 2013

Total: 38 samples

As of Oct. 1, 2013

Total: 84 samples

- All tested samples were met to non-cleanable contamination specification.
Outline

1. Current Status of Resist Outgas Qualification

2. Proposal on XPS Measurement Condition (Co-work with NIST & ASML)

3. Impact of Mask Open Ratio

4. Other Topics (Co-work with Univ. of Hyogo)

5. Summary
Sulfur Desorption Study for Power / Neutralizer

- S desorption was **not observed** at 4 sequential tests with **low power mode**.
- S desorption was **observed** at 2 sequential tests with **high power mode**.
- S desorption depend on 'x-ray dose' or 'high power x-ray & neutralizer combination.'
### Collaboration with NIST & ASML for XPS Measurement

#### XPS Conditions at NIST and EIDEC

<table>
<thead>
<tr>
<th></th>
<th>EIDEC Low Power Mode (current condition)</th>
<th>EIDEC High Power Mode</th>
<th>NIST</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Model</strong></td>
<td>PHI5000 VersaProbe II (ULVAC PHI)</td>
<td></td>
<td>AXIS-Ultra DLD (KRATOS)</td>
</tr>
<tr>
<td><strong>X-ray Source</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>X-ray Irradiated Area</strong></td>
<td>0.031mm$^2$ (200μm φ)</td>
<td>0.008mm$^2$ (100μm φ)</td>
<td>6mm$^2$</td>
</tr>
<tr>
<td><strong>X-ray power</strong></td>
<td>1.6kW/mm$^2$</td>
<td>12.7kW/mm$^2$</td>
<td>0.023kW/mm$^2$</td>
</tr>
<tr>
<td><strong>X-ray power ratio</strong></td>
<td>1</td>
<td>8</td>
<td>1/70</td>
</tr>
<tr>
<td><strong>Electron Neutralizer</strong></td>
<td>On/Off</td>
<td>On/Off</td>
<td>Off</td>
</tr>
<tr>
<td><strong>Ar$^+$ Ion Neutralizer</strong></td>
<td>On/Off</td>
<td>On/Off</td>
<td>Not available</td>
</tr>
</tbody>
</table>

- XPS conditions are different between NIST and EIDEC.
- The impact of x-ray power and neutralizer was investigated with NIST and ASML.
The Effect of Power / Neutralizer on Sulfur Measurement

**EIDEC**
- Sample: Sulfur rich sample (WS-S)
- Measurement Date: April 2013
- X-ray Power: 1.6kW/mm² or 12.7kW/mm²
- Measurement Time: 20 min.

**NIST**
- Sample: Sulfur rich sample (WS-S)
- Measurement Date: July 2013
- X-ray Power: 0.023kW/mm²
- Measurement Time: 1200 min. (=17 min. at EIDEC low power mode)

**Contamination Components (WS027)**

<table>
<thead>
<tr>
<th></th>
<th>F1s</th>
<th>Si2s</th>
<th>P2p</th>
<th>S2p</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low-Pw, E-off, I-off</td>
<td>0.5</td>
<td>0.2</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Low-Pw, E-on, I-off</td>
<td>2.0</td>
<td>1.4</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Low-Pw, E-on, I-on</td>
<td>2.1</td>
<td>1.9</td>
<td>0.4</td>
<td>0.7</td>
</tr>
<tr>
<td>High-Pw, E-on, I-on</td>
<td>2.6</td>
<td>2.7</td>
<td>0.3</td>
<td>0.7</td>
</tr>
</tbody>
</table>

**WS027 S Concentration**

- NIST-measured area
- EIDEC-measured area

- S desorption was not observed at either test site when neutralizer was not used.
### EIDEC
- Sample: Fluorine rich witness sample (WS-F)
- Measurement Date: April 2013
- X-ray Power: 1.6kW/mm² or 12.7kW/mm²
- Measurement Time: 20 min.

### NIST
- Sample: Fluorine rich witness sample (WS-F)
- Measurement Date: July 2013
- X-ray Power: 0.023kW/mm²
- Measurement Time: **1200 min.**

### Contamination Components (WS023)

<table>
<thead>
<tr>
<th>Component</th>
<th>Measurement Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si2s</td>
<td>2.2</td>
</tr>
<tr>
<td>P2p</td>
<td>1.8</td>
</tr>
<tr>
<td>S2p</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>1.6</td>
</tr>
</tbody>
</table>

### F₁s

- Analysis position at EIDEC
- Analysis positions at NIST

### F desorption

- F desorption was observed at both test sites.

---

**Graphs:**

- **WS023 F Concentration**
- **XPS measurement time vs. F**

---

IEUVI Resist TWG, Toyama, Japan  Oct. 6, 2013
Summary of XPS Measurement Condition

**Sulfur**

- Higher power x-ray in combined with neutralizer strongly desorbed Sulfur.
- No significant change was observed in Sulfur with x-ray dose without neutralizer.

**Fluorine**

- Higher power x-ray in combined with neutralizer strongly desorbed Fluorine.
- Significant x-ray-induced desorption was observed from NIST data

→ Don’t use neutralizer with higher x-ray power!
→ Use x-ray with the dose less than this experiment!
Outline

1. Current Status of Resist Outgas Qualification

2. Proposal on XPS Measurement Condition
   (Co-work with NIST & ASML)

3. Impact of Mask Open Ratio

4. Other Topics
   (Co-work with Univ. of Hyogo)

5. Summary
# Impact of Mask Opening Ratio on Outgassing

<table>
<thead>
<tr>
<th>Mask</th>
<th>Total Exposed Area</th>
<th>Acceptable Outgas Amount/area</th>
<th>Total Outgassing Amount</th>
<th>Contamination Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>$S_w$</td>
<td>$G$</td>
<td>$T_o$</td>
<td>$T_c$</td>
</tr>
<tr>
<td>0.1xS</td>
<td>$0.1xS_w$</td>
<td>$10xG$</td>
<td>$T_o$</td>
<td>$T_c$</td>
</tr>
</tbody>
</table>

- Resist suppliers develop level specific resists for obtaining level specific performances. For example, the resist for hole structures is printed only by hole reticles which have small opening ratio.
- It suggests there is a possibility to have level specific outgas criteria and/or level specific QC period for level specific resist.
Outline

1. Current Status of Resist Outgas Qualification

2. Proposal on XPS Measurement Condition (Co-work with NIST & ASML)

3. Impact of Mask Open Ratio

4. Other Topics (Co-work with Univ. of Hyogo)

5. Summary
### Contribution of Outgas Species on CG

#### Model Resists prepared at EIDEC

<table>
<thead>
<tr>
<th>Code.</th>
<th>Sample Concept</th>
<th>Polymer</th>
<th>PAG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>Standard resist</td>
<td><img src="" alt="Polymer Structure" /></td>
<td><img src="" alt="PAG Structure" /></td>
</tr>
<tr>
<td>Sample A</td>
<td>Contribution of PU</td>
<td>Acid labile unit</td>
<td>none</td>
</tr>
<tr>
<td>Sample B</td>
<td>Contribution of PAG</td>
<td>Acid stable unit</td>
<td><img src="" alt="PAG Structure" /></td>
</tr>
</tbody>
</table>

#### Cleanable Contamination thickness

<table>
<thead>
<tr>
<th></th>
<th>Under same dose condition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EUV</td>
</tr>
<tr>
<td>Background</td>
<td>0.12</td>
</tr>
<tr>
<td>Control</td>
<td>1.00</td>
</tr>
<tr>
<td>Sample A</td>
<td>0.08</td>
</tr>
<tr>
<td>Sample B</td>
<td>0.80</td>
</tr>
</tbody>
</table>

- No outgassing is observed for Sample A. PU is not de-protected by only EUV or EB exposure.
- Comparing CG of Sample B to that of control, PAG contribution to the CG height is calculated 80~85% in case of this model resist.
- To reduce resist outgassing, the material design of PAG is essential.
Cation bound system showed less outgassing than that of PAG blend and anion bound systems.

To reduce the outgassing, PAG cation structure must be modified.


Oct. 6, Poster session Toshiya Takahashi, P-RE-58 “Cleanability of resist-outgas non-carbon contaminations using hydrogen radical cleaning”
Summary

- EIDEC has got certification of outgas testing from ASML in July and is gradually building up more and more work. Current estimated capacity is 30-40 samples/month.

- EIDEC collaborated with NIST and ASML on XPS condition. We suggested that you should not use neutralizer with higher x-ray power and not to use x-ray with the dose less than this experiment.

- Mask open ratio changes total outgas amount per wafer. It suggests there is a possibility to have level specific outgas criteria for level specific resist.

- EIDEC will present three papers in EUVL Symposium 2013. It turns out outgassing from PAG have largest contribution to the cleanable contamination. PAG cation structure should be modified in order to reduce the outgassing.
Acknowledgement

This work is supported by New Energy and Industrial Technology Development Organization (NEDO).

We would like to thank EIDEC member companies.

Thank you.