Update of Resist Outgas Testing at EIDEC

Eishi Shiobara,
EUVL Infrastructure Development Center, Inc.
Status of Resist Outgas Testing

Announcement of the relaxation of resist outgassing spec from ASML at the end of Feb. 2015.

- Traditional Chemically Amplified Resist (CAR)
  - No outgas spec for cleanable and non-cleanable contamination (Monitoring during 2015)
  - All traditional CAR can be evaluated in EUV scanner without testing.

<table>
<thead>
<tr>
<th>Outgassing Spec</th>
<th>Cleanable Contamination</th>
<th>Non-cleanable Contamination</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; Q1/2014</td>
<td>&lt; 3 nm</td>
<td>&lt; 0.16%</td>
</tr>
<tr>
<td>&lt; Q1/2015</td>
<td>&lt;10 nm</td>
<td>&lt; 0.16%</td>
</tr>
<tr>
<td>&gt; Q1/2015</td>
<td>no spec</td>
<td>no spec</td>
</tr>
</tbody>
</table>

- Non-CAR (Alternative Resist)
  - Non-CAR litho evaluation in EUV scanner is available with waiver.
  - Outgassing research is required with test conditions of:
    ✓ EUV light for WS and wafer
    ✓ Hydrogen environment, .....
Basic Infrastructures for Resist Outgas Testing at EIDEC

- EB-based outgas tester is working for resist outgas qualification.
- EIDEC keeps the activity of both EB-based and EUV-based tester in FY 2015.
Almost 400 costumer samples have been evaluated so far.
The number of samples with > 10nm contamination growth (CG) is increasing.
All samples tested showed the reflectivity loss of <0.16%.
Recent Result of Cleanable Contamination

Feb.26 – Sep. 25

Total: 42 samples

- Over 40 customer samples have been evaluated.
- 1/3 of samples tested showed over 10nm CG.
- The number of samples with high CG is increasing.
Benefit of Outgas Spec Relaxation

Enlargement of the flexibility of material design for traditional CAR against the trade-off among RLS

Resolution (R) \hspace{1cm} \text{Sensitivity (S)}

LWR \hspace{1cm} < Q1/2014 \hspace{1cm} R \hspace{1cm} < Q1/2015 \hspace{1cm} S \hspace{1cm} > Q1/2015

Removal of outgas spec for resist evaluation at EUV scanner can accelerate the development of CAR.
Position of Outgassing in Resist Selection

Resist outgassing becomes one of the resist properties, not specification.

- Sensitivity
- Resolution
- Focus margin
- Dose margin
- LWR
- CD uniformity
- Resist profile
- Defectivity
- Etch durability
- Lifetime
- Outgassing

The device manufacturers can select EUV resists considering outgas property, comparing with the other resist properties.
Status of Resist Outgas Testing

Announcement of the relaxation of resist outgassing spec from ASML at the end of Feb. 2015.

- Traditional Chemically Amplified Resist (CAR)
  - No outgas spec for cleanable and non-cleanable contamination (Monitoring during 2015)
  - All traditional CAR can be evaluated in EUV scanner without testing.

<table>
<thead>
<tr>
<th>Outgassing Spec</th>
<th>Cleanable Contamination</th>
<th>Non-cleanable Contamination</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; Q1/2014</td>
<td>&lt; 3 nm</td>
<td>&lt; 0.16%</td>
</tr>
<tr>
<td>&lt; Q1/2015</td>
<td>&lt; 10 nm</td>
<td>&lt; 0.16%</td>
</tr>
<tr>
<td>&gt; Q1/2015</td>
<td>no spec</td>
<td>no spec</td>
</tr>
</tbody>
</table>

- Non-CAR (Alternative Resist)
  - Non-CAR litho evaluation in EUV scanner is available with waiver.
  - Outgassing research is required with test conditions of:
    - EUV light for WS and wafer
    - Hydrogen environment, .....
Chemical Reactions in EUV Resist Process Flow

**CAR**

- Coating
- Post coating
- Bake
- Exposure
- Post exposure
- Bake
- Development

**Non-CAR**

- Coating
- Post Coating
- Bake
- Exposure
- Post exposure
- Bake
- Development

- Main chemical reactions are considered to be occurred in the exposure process for non-CAR.
- It might be the risk to induce highly outgassing during exposure for non-CAR.
Concerns of Non-CAR Outgassing in H₂ Environment

1. Hydrogen radicals react with the metal elements in Non-CAR?
2. Metal hydrides outgas from the resist?
3. Metal hydride outgas species deposit on EUV mirror?
**Metal Containing Model Samples**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Metal Compounds</th>
<th>PAG</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Hf 4+ Hafnium carboxyethyl acrylate</td>
<td>No PAG</td>
<td>Butanol, PGMEA, PGME</td>
</tr>
<tr>
<td>B</td>
<td>PAG1: TPS-nonaflate 11 wt% (13mol%)</td>
<td>Butanol, PGMEA, PGME</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>PAG2: Naphtyl-nonaflate 12 wt% (13mol%)</td>
<td>Butanol, PGMEA, PGME</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>Dibutoxy Zirconium bis(ethy lacetoacetato)</td>
<td>No PAG</td>
<td>Butanol, PGMEA, PGME</td>
</tr>
<tr>
<td>E</td>
<td>PAG1: TPS-nonaflate 5 wt% (4.4mol%)</td>
<td>Butanol, PGMEA, PGME</td>
<td></td>
</tr>
</tbody>
</table>

- **EIDEC prepared metal containing model samples for detail outgas analysis.**
Contamination growth (CG) was observed by metal containing samples.
Remarkable CG increase were observed by PAG loading comparing to CAR.
XPS Measurement of Witness Sample

**Hf + PAG1 (Sample B) without cleaning**

Outgas tester: HERC

**Zr + PAG1 (Sample E) without cleaning**

Hf was not observed

Zr was not observed
Key Items for Non-CAR Outgas Testing

<table>
<thead>
<tr>
<th>Key Items for non-CAR outgas testing</th>
<th>HPEUV (EUV-based)</th>
<th>HERC (EUV-based)</th>
<th>EUVOM (EB-based)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EUV to WS and wafer</td>
<td>○</td>
<td>○</td>
<td>×</td>
</tr>
<tr>
<td>- To WS</td>
<td>EUV</td>
<td>EUV</td>
<td>EB</td>
</tr>
<tr>
<td>- To wafer</td>
<td>EUV</td>
<td>EUV</td>
<td>EB</td>
</tr>
<tr>
<td>H$_2$ environment</td>
<td>× ⇒ ○</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>Simulating EUV exposures</td>
<td>○</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>- Pump speed</td>
<td>○</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>- Stage velocity</td>
<td>○</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>- Multiple wafer</td>
<td>○</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>Temperature control</td>
<td>○</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>XPS and SE</td>
<td>○</td>
<td>○</td>
<td>○</td>
</tr>
</tbody>
</table>

- High power EUV irradiation tool (HPEUV) had satisfied the key items non-CAR testing except for H$_2$ environment.
- EIDEC has prepared non-CAR outgas test setup in H$_2$ at HPEUV.
Basic Configuration of HPEUV

High Power EUV Irradiation Tool (HPEUV)

- The relay mirrors is reduced to obtain high EUV power on wafer.
- The 10W EUV source for HPUV is sufficient to mimic the power density of HVM scanner with 250W source.
Verification of $\text{H}_2$ Pressure for Non-CAR Testing

H$_2$ pressure during test flow

- H$_2$ pressure of 100Pa during EUV exposure was confirmed.
- Functionality of multiple wafer exposure was available.

Test setup at HPEUV

RGA spectrum during test flow

Only H$_2$ (amu=2)
CG of Metal Containing Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Metal Compounds</th>
<th>PAG</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>Hf carboxyethyl acrylate</td>
<td>10 wt%</td>
</tr>
</tbody>
</table>

- EUV power on WS: 900mW/cm²
- EUV power on Wafer: 900mW/cm²
- Exposure dose = 27mJ/cm²

**In H₂ of 100Pa**

Contamination thickness: 0.50nm (max)

**In Vacuum**

Contamination thickness: 0.38nm (max)

- Preliminary result of outgas testing in H₂ was obtained using metal containing model sample.
- Significant difference between in H₂ and in vacuum was not observed.
RGA Spectrum of Metal Containing Samples

Sample B

In $\text{H}_2$ of 100Pa

(Use differential pumping)

In Vacuum

• RGA in $\text{H}_2$ could observe some peaks of outgas species from the metal containing sample.
Summary

- EIDEC keeps the activities of both basic EB-based tester and basic EUV-based in FY 2015.
- Over 40 of costumer samples was evaluated from the last TWG meeting and the number of high CG samples is increasing.
- EIDEC has prepared metal containing model samples for open discussion of outgas detail analysis.
- It was found CG of the metal containing model samples was larger than that of conventional CAR when PAG was loaded.
- Metal related contaminations of the metal containing model samples were not found by XPS analysis of WS.
- Test setup for non-CAR outgas testing in H₂ was prepared at HPEUV.
- Preliminary result of outgas testing in H₂ was obtained using the metal containing model samples by HPEUV, and detail analysis is ongoing.
Presentations for Resist Outgas Research from EIDEC

- E. Shiobara, et al., “Recent progress in resist outgas testing for the new platform at EIDEC” P-OC-05, Poster: Outgas and Contamination Monitoring

Acknowledgement

This work was supported by Ministry of Economy, Trade and Industry (METI) and New Energy and Industrial Technology Development Organization (NEDO).
Special Thanks to

Shinji Mikami, Yukiko Kikuchi, Takeshi Sasami, Takashi Kamizono, Shinya Minegishi, Toru Fujimori, Junichi Furukawa, Yosuke Ohta, Toru Kasuya, Satoshi Tanaka and Member companies

Takeo Watanabe, Tetsuo Harada, Hiroo Kinoshita

Yu Jen Fan

Robert Berg, Shannon Hill, Charles Tarrio, Thomas Lucatorto

Ivan Pollentier

Gijsbert Rispens, Oktay Yildirim, Raymond Maas, Coen Verspaget
Thank you!!