New approach for reducing the Out of Band effect and outgassing by applying top coat materials

(Outgassing and Out-of Band Protection Layer: OBPL)

Nissan Chemical Industries, LTD.
Outline

Lithography Technology

130nm  90nm  65nm  45nm  32nm  22nm  16nm

KrF  ArF  ArF Imm.  DPT  EUV, EB

Nissan Chemical’s activity for EUVL

Today’s talk

2013 International Workshop on EUV Lithography, in Maui
Nissan OBPL
OBPL

**Outgassing & Out-of-Band Protection Layer**

- **Outgassing barrier**
- **Out-of-Band filter**

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2013 International Workshop on EUV Lithography, in Maui
Concept of Top Coat material

Characteristic of OBPL:

1. Low transmittance for OoB light
2. High transmittance for EUV light
3. Prevention of outgassing from resist
4. No mixing with resist film
5. Removable by development and rinse process

Outgassing and OoB Protection Layer (OBPL)
Resist
Under layer

Specific property for EUVL
Common property with TARC and imm. TC
Material design Concept

- **Ridged unit**: high outgassing barrier property and DUV abs.
- **Solubility unit A**: Developable unit into TMAH/DIW (For PTI)
- **Solubility unit B**: Solubility unit for OBPL Solvent (org.Solvent) and NBA (For NTI)
Development road map

1\textsuperscript{st} Generation

<table>
<thead>
<tr>
<th>Polymer platform</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td>OoB absorption</td>
<td>😞</td>
</tr>
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<td>Outgassing barrier</td>
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<tr>
<td>Litho improvement</td>
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<tr>
<td>Applicable for resist</td>
<td>Pure methacryl</td>
</tr>
<tr>
<td>Applicable for Dev. process</td>
<td>PTD</td>
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2\textsuperscript{nd} Generation

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<th>Polymer platform</th>
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3\textsuperscript{rd} Generation (Current R&D)

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<td>All resist type</td>
</tr>
<tr>
<td>Applicable for Dev. process</td>
<td>PTD &amp; NTD</td>
</tr>
</tbody>
</table>
Outgassing
### PSN in EUVL

<table>
<thead>
<tr>
<th>HP of L/S</th>
<th>EUV (LBNL MET)</th>
<th>EB (50 keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 nm</td>
<td>--</td>
<td>205</td>
</tr>
<tr>
<td>20 nm</td>
<td>1360</td>
<td>500</td>
</tr>
<tr>
<td>15 nm</td>
<td>2040</td>
<td>--</td>
</tr>
<tr>
<td>11 nm</td>
<td>2720 (estimated)</td>
<td>--</td>
</tr>
</tbody>
</table>

**20 mJ/cm² for 20 nm, 30 mJ/cm² for 15 nm are required**
Resolution – sensitivity tradeoff

PSN statistics causes res. – sens. tradeoff

Res. ⇒ Large photon cts. is preferable
Sens. ⇒ Small is preferable
LWR

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Resolution – outgassing tradeoff

Same polymer, PAG and PAG loading

Spec out

Calc. Esize (mJ/cm²)

Relative contamination thick. (nm)

[Q] x 4.0

[Q] x 1.4

[Q] x 1.0

Better resolution

Slow Esize. for high res (1x nm). caused outgassing

EUV

R₁

M⁺

R₂

R₃

Volatile
Low Mw species

Increasing dose

Increasing outgassing

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Important message

Below Hp15 Generation.

More than 2000 photon will be required to get

The enough Resolution and imaging quality.

→ High dose (>30mJ) will be exposed to PR.

→→ Outgass must be higher and higher.

Because of trade off between Res. & Outgass.

EUV-TC will be required for Hp15 and beyond
## Previous study by RGA

<table>
<thead>
<tr>
<th>Polymer platform</th>
<th>OBPL-1</th>
<th>OBPL-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rigid type</td>
<td>1.21</td>
<td>Flexible type</td>
</tr>
</tbody>
</table>

<table>
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<tr>
<th>Film density (g/cm³)</th>
<th>OBPL-1</th>
<th>OBPL-2</th>
</tr>
</thead>
<tbody>
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<td>1.21</td>
<td>Flexible type</td>
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**PR Outgassing rate through OBPL (%):**

- **Benzene (PAG-delivered):**
  - **PR-A:**
    - **Rigid OBPL on PR-A:** 1.8%
    - **Flexible OBPL on PR-A:** 17.2%

**Chemistry dependency for outgass barrier was confirmed, But applying OBPL could reduce the outgassing significantly.**
Outgassing barrier test by WS

Tester / location: CNSE ROX (Witness)
OBPL-A (FT: 30nm)

<table>
<thead>
<tr>
<th>Carbon contamination thickness (nm)</th>
<th>Cleanable CG.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5nm</td>
<td></td>
</tr>
<tr>
<td>0.21nm</td>
<td>Maximum allowable value for NXE3100 and NXE3300</td>
</tr>
</tbody>
</table>

There is no significant difference in outgassing level
By using OBPL for optimized PR.
Outgassing barrier test

Model PR

Low Ea, high CG

6.74nm

Carbon contamination thickness (nm)

7
6
5
4
3
2
1
0

Resist-B
(Model EUV-PR.
High outgassing PR)

OBPL-B/ Resist-B
(OBPL: 3rd. Gen.)

0.01nm

Cleanable CG.

Applying OBPL

Maximum allowable value for NXE3100 and NXE3300

Perfect outgassing prevention by OBPL was confirmed.

→ SPEC-OUT PR could be SPEC-IN by Applying OBPL.
Contamination distributional analysis

Analysis method: Depth profile
Tool: TOF-SIMS
Detection atom: Sulfur
Variation concentration of Sulfur atom

Flexible OBPL

Rigid OBPL

Rigid OBPL blocks PR outgassing at interface.
OoB study
**Requirement of OBPL**

- Low DUV transmittance: 20~30%@min.
- High EUV transmittance: ~90%

Diagram showing:
- DUV transmittance
- EUV transmittance
- OBPL: 30nm

Graphs illustrating transmittance percentages against wavelength and film thickness.
Investigation of OBPL effect

1. Reference
   - PR coat
   - EUV exp.
   - PEB
   - Dev.

2. OoB influence
   - PR coat
   - OoB exp.
   - EUV exp.
   - PEB
   - Dev.

3. Applying OBPL
   - PR coat
   - OBPL coat
   - EUV exp.
   - PEB
   - Dev.

4. OBPL effect
   - PR coat
   - OBPL coat
   - OoB exp.
   - EUV exp.
   - PEB
   - Dev.

OoB exposure condition
- Wavelength: 160~300nm (broad band)
- Dose: 5.0mJ/cm² (20% of EUV)

S.A.George et al., SPIE (2011)
OBPL effect results

**EUV**
- Dose : 26.8mJ/cm²
- LWR : 4.17nm

**EUV + OoB**
- Dose : 18.7mJ/cm²
- LWR : 6.32nm

**OBPL**
- Dose : 28.6mJ/cm²
- LWR : 4.25nm

OBPL behaves extremely well as OoB filter.

- Dose : 26.8mJ/cm²
- LWR : 4.10nm
### 3rd Generation (Current R&D)

**Concept: Universal TC for PR and process**

<table>
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<th>Feature</th>
<th>Description</th>
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Lithographic performance with NXE:3100

2nd Gen. OBPL

without OBPL

CD : 27.7nm
Dose : 11.2mJ/cm²
LWR : 6.4nm
DOF : 0.20um

with OBPL

CD : 27.4nm
Dose : 11.5mJ/cm²
LWR : 6.6nm
DOF : 0.22um

2nd gen. OBPL showed good compatibility with Methacrylate PR.
But, only with Methacrylate PR.
**3\textsuperscript{rd} Generation OBPL**

**Target:**
Universal compatibility for PR (Methacrylate & PHS) and Dev. Process (PTD&NTD).

### Material design

- **Rigid unit**
- **Outgassing barrier**
- **Hydrophilic unit**
- **Solubility unit for solvent**
- **Functional unit**

### Sample design

<table>
<thead>
<tr>
<th>Basis of materials</th>
<th>Process</th>
</tr>
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<tbody>
<tr>
<td>High rigidity resin</td>
<td>All resist type</td>
</tr>
<tr>
<td><strong>Solvent</strong></td>
<td><strong>PTD (TMAH aq) &amp; NTD (NBA)</strong></td>
</tr>
<tr>
<td><strong>Org. Solvent</strong></td>
<td></td>
</tr>
<tr>
<td>(non-mixing with Methacryl and PHS type PR)</td>
<td></td>
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$x+y = 100\%$
Proposal sample (3rd Generation)

Material design

Sample property (NCX2088)

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Polymer platform</th>
<th>R unit</th>
<th>Outgassing qualification</th>
<th>Transmittance</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCX2088</td>
<td>B</td>
<td>High hydrophilic</td>
<td>Pass</td>
<td>81% 43%</td>
</tr>
</tbody>
</table>

High DUV abs. and good outgass barrier property
Methacrylate type PR

Tester / location: Sematech (AMET)

Focus

Resist-C

NCX2088 / Resist-C

Appling OBPL keep good process margin and LWR.

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HS/Methacrylate hybrid type

Tester / location: Sematech (AMET)

Resist-D

| CD (nm) | 26.1 |
| Dose(mJ/cm²) | 24.0 |
| LWR (nm) | 4.0 |
| Max EL (%) | > 29.2 |
| Max DOF (um) | > 0.30 |

NCX2088 / Resist-D

| CD | 25.7 |
| Dose | 27.0 |
| LWR | 4.1 |
| Max EL | > 18.5 |
| Max DOF | > 0.30 |

Applying OBPL keep good process margin and LWR.

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Performance for NTI

Lithography performance

Outgassing barrier performance

H. tsubaki, SPIE 2013

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Summary

Outgassing

Perfect barrier property was confirmed. ROX qualification of Staked (PR/OBPL), SPEC-OUT PR could be SPEC-IN by OBPL!!

Universality
PR kinds and Process

Methacrylate type PR(PTI)
PHS hybrid type PR (PTI)
PHS hybrid type PR(NTI)

3rd Gen. OBPL

NCX2088

OoB

High DUV abs. could prevent OoB irradiation effect.
Conclusion

- Nissan Chemical has successfully developed OBPL for EUVL.

- OBPL has PR outgassing barrier property and Out-of-Band filter effect.

- 3rd Gen. OBPL showed good PR universality and process compatibility.

- OBPL can be the key material for high volume manufacturing by EUVL.