DDR Process and Materials for NTD Photo Resist toward 1Xnm Patterning and beyond

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Nissan Chemical, -where unique & solution meet-

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Semiconductor Materials Research Department
Outline

About DDR process

About DDR process and material for NTD PR

Patterning data
  - Pattern reverse from L/S into L/S
  - Pattern reverse from pillar into C/H

Summary
About DDR process

About DDR process and material for NTD PR

Patterning data
- Pattern reverse from L/S into L/S
- Pattern reverse from pillar into C/H

Summary
Some lithography techniques have been demonstrated to create fine pattern.

EUV lithography is one of the candidate for next gen. lithography.
### Difficulty in current process

#### Process step

<table>
<thead>
<tr>
<th>Thin PR</th>
<th>Thick PR</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ideal</strong></td>
<td><strong>Actual</strong></td>
</tr>
</tbody>
</table>

#### Lithography

- **PR**
  - HM 1
  - HM 2
  - Sub.

- **Can’t open HM...**

#### Pattern transfer

- **Can’t transfer...**

**Thick PR is prefer to achieve pattern transfer.**

⇒ **Thicker PR cause pattern collapse...**

**Dry process** is one of the solution to overcome this trade-off.
Dry process

sc CO2 Dry Development

Wet Development

sc CO2

No capillary force

DSA (Directed Self-Assembly)
【Pattern creation by Dry Etching】

No capillary force

L0 = 30nm

Dry process can create fine pattern with high aspect ratio.

→ NissanChemical also has Dry process 【DDR Process】
Dry Development Rinse process

Current process (wet dev.)

Exposure → PEB → Development, Rinse & Spin dry

DDR process: Dry Development Rinse process

Exposure → PEB → Development & Rinse

Replacement by DDR material

Key Process

- DDRM -Si polymer

- Image reversal
- Collapse free process
- Easy pattern transfer
- Special tools unnecessary
Current progress for DDR process

NCR500 (80nm)

DDR specialized EUV PR (70nm)

Nissan Std. Si-HM

8nm Line (Pitch 32mn)

Line CD : 8.3nm
LER : 2.5nm

DDR FTK : 23.9nm

Aspect ratio : 2.9

Progress for single nm resolution by applying Dry development rinse process (DDRP) and materials (DDRM)
Presenter : Wataru Shibayama (Poster)

22hp Reversed pillar

How about NTD PR?
About DDR process

About DDR process and material for NTD PR

Patterning data
  - Pattern reverse from L/S into L/S
  - Pattern reverse from pillar into C/H

Summary
**NTD process**

Exposure $\rightarrow$ Baking (de-protection) $\rightarrow$ Development

<table>
<thead>
<tr>
<th>Exposure</th>
<th>Baking (de-protection)</th>
<th>Development</th>
</tr>
</thead>
<tbody>
<tr>
<td>OR</td>
<td>OH</td>
<td>PTD (TMAH aq.)</td>
</tr>
<tr>
<td>OR</td>
<td>OH</td>
<td>NTD (Org. solv.)</td>
</tr>
</tbody>
</table>

- **EUV**
  - 14nm L/S<sup>1</sup>
  - 37mJ/cm<sup>2</sup>

- **EUV**
  - 21nm block<sup>1</sup>
  - 18mJ/cm<sup>2</sup>

1) Proc. of SPIE, Negative-tone imaging with EUV exposure toward 13 nm hp, Fujifilm

Current NTD PR shows almost same performance compared to PTD-PR.
Merit of NTD-DDR process

In EUVL, dark field mask is the preferred because of defectivity, flare

Target: Fine Trench, C/H

- C/H or trench can be created by NTD-DDR process with high quality.
- It becomes easy to achieve pattern transfer due to using DDRM as HM.

Blight mask

Defect

NTD only

Dark mask

Defect

NTD image

Pattern image got worse
- Flare
- Defect printing

NTD & Image reversal

Defect

NTD image

image reversal

Thick DDRM
**DDR Material for NTD PR**

**Dry Development Rinse Material : DDRM**

**Solvent type**

<table>
<thead>
<tr>
<th>Etch Selectivity vs. PR</th>
<th>CF&lt;sub&gt;4&lt;/sub&gt;</th>
<th>O&lt;sub&gt;2&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic (For NTD)</td>
<td>1.1</td>
<td>&lt; 0.05</td>
</tr>
</tbody>
</table>

**Requirement:**
- High compatibility for organic developer
- No mixing to NTD PR
- Gap filling in narrow pitch
**Candidate of DDRM for NTD PR**

<table>
<thead>
<tr>
<th>Sample</th>
<th>NCR541</th>
<th>NCR581</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Generation</strong></td>
<td>2&lt;sup&gt;nd&lt;/sup&gt; gen.</td>
<td>3&lt;sup&gt;rd&lt;/sup&gt; gen.</td>
</tr>
<tr>
<td><strong>Polymer</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>R1, R2 : Solubility for org. solv.</td>
<td>R1 : Solubility for org. solv.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R3 : High cross-link density</td>
</tr>
<tr>
<td><strong>Functional unit</strong></td>
<td>Org. solvent A</td>
<td>Org. solvent A</td>
</tr>
<tr>
<td><strong>Solvent</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Si content (Normalized)</strong></td>
<td>1.0</td>
<td>1.2</td>
</tr>
</tbody>
</table>
Study of mixing layer

ToF-SIMS (Depth direction)

- DDRMs (90nm)
- Exposed PR-B (60nm)

DDRM removal by developer

XPS (Surface)

- Exposed PR-B (60nm)

<table>
<thead>
<tr>
<th>Remaining film</th>
<th>Removed film</th>
<th>ΔF.T. (F.T.A - F.T.B)</th>
<th>XPS (atom%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PR-B</td>
<td>-</td>
<td>-0.3nm</td>
<td>C</td>
</tr>
<tr>
<td>DDRMs</td>
<td>-</td>
<td>-</td>
<td>20</td>
</tr>
<tr>
<td>PR-B</td>
<td>Ref. DDRM</td>
<td>-30.0nm</td>
<td>57.9</td>
</tr>
<tr>
<td>PR-B</td>
<td>NCR541</td>
<td>-1.2nm</td>
<td>72.6</td>
</tr>
<tr>
<td>PR-B</td>
<td>NCR581</td>
<td>-1.8nm</td>
<td>73.8</td>
</tr>
</tbody>
</table>

Mixing level: Low

2) PR-B: imec STD, NTD-EUV PR

EUVL Symposium 2016, Hiroshima, Japan
About DDR process

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Patterning data
- Pattern reverse from L/S into L/S
- Pattern reverse from pillar into C/H

Summary
### Patterning @hp14~18nm

<table>
<thead>
<tr>
<th></th>
<th>hp18nm</th>
<th>hp15nm</th>
<th>hp14nm</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Normal NTD</strong></td>
<td><img src="hp18nm_normal_ntd.png" alt="Image" /></td>
<td><img src="hp15nm_normal_ntd.png" alt="Image" /></td>
<td><img src="hp14nm_normal_ntd.png" alt="Image" /></td>
</tr>
<tr>
<td></td>
<td><em>(w/o rinse)</em></td>
<td><em>(w/o rinse)</em></td>
<td><em>(w/o rinse)</em></td>
</tr>
<tr>
<td><strong>PR-B (Fujifilm, 40nm)</strong></td>
<td><img src="hp18nm_pr_b.png" alt="Image" /></td>
<td><img src="hp15nm_pr_b.png" alt="Image" /></td>
<td><img src="hp14nm_pr_b.png" alt="Image" /></td>
</tr>
<tr>
<td><strong>NCR541</strong></td>
<td><img src="hp18nm_ncr541.png" alt="Image" /></td>
<td><img src="hp15nm_ncr541.png" alt="Image" /></td>
<td><img src="hp14nm_ncr541.png" alt="Image" /></td>
</tr>
<tr>
<td><strong>Previous DDRM</strong></td>
<td><img src="hp18nm_previous_ddrm.png" alt="Image" /></td>
<td><img src="hp15nm_previous_ddrm.png" alt="Image" /></td>
<td><img src="hp14nm_previous_ddrm.png" alt="Image" /></td>
</tr>
<tr>
<td><strong>NCR581</strong></td>
<td><img src="hp18nm_ncr581.png" alt="Image" /></td>
<td><img src="hp15nm_ncr581.png" alt="Image" /></td>
<td><img src="hp14nm_ncr581.png" alt="Image" /></td>
</tr>
<tr>
<td><strong>High cross-link type</strong></td>
<td><img src="hp18nm_high_cross.png" alt="Image" /></td>
<td><img src="hp15nm_high_cross.png" alt="Image" /></td>
<td><img src="hp14nm_high_cross.png" alt="Image" /></td>
</tr>
</tbody>
</table>

High cross link type DDRM showed good patterning property.

NXE3300 (imec), NA: 0.33
Pattern wigging after etching

<table>
<thead>
<tr>
<th>Property</th>
<th>NCR541</th>
<th>NCR581</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixing level</td>
<td>1.0 – 1.5nm</td>
<td></td>
</tr>
<tr>
<td>Si content (Normalized)</td>
<td>1.0</td>
<td>1.2</td>
</tr>
<tr>
<td>Film density (Normalized)</td>
<td>1.0</td>
<td>1.1</td>
</tr>
<tr>
<td>$O_2$ Etch rate (Normalized)</td>
<td>1.0</td>
<td>&lt; 0.5</td>
</tr>
</tbody>
</table>

Etch damage
- Low cross-link
- Soft pattern

Low etch damage
- High cross-link
- Rigid pattern
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**Patterning data**
- Pattern reverse from L/S into L/S
- Pattern reverse from pillar into C/H

**Summary**
Comparison of LCDU

CD size 30nm / Pitch 52nm, PR-B, F.T. : 40nm

PTD C/H (imec STD)
- Ave. CD: 32.2nm
- Range: 1.6nm
- 3σ: 1.5nm

NTD Pillar (PR-B, imec STD)
- Ave. CD: 32.1nm
- Range: 1.9nm
- 3σ: 0.8nm

NTD Pillar → C/H (NCR581)
- Ave. CD: 28.7nm
- Range: 1.9nm
- 3σ: 1.5nm

NXE3300 (imec), NA: 0.33

Rev. C/H of DDRM showed same LCDU compared to PTD C/H in EUVL. There were still gap compared to original pillar.
Dependence of pattern shape

To use thicker PR and to apply enough etch back are useful for good LCDU.
Dependence of PR thickness

Pillar 30nm / Pitch 60nm, PR-B, F.T. : 40~80nm

EB tool (Elionix), 130kV, 50pA

Ave. CD: 25.7nm  
Max CD: 26.5nm  
Min CD: 24.9nm  
Range: 1.6nm  
3σ: 1.1nm

Ave. CD: 27.4 nm  
Max CD: 27.9nm  
Min CD: 26.9nm  
Range: 1.0nm  
3σ: 0.8nm

Ave. CD: (29.7nm)  
Max CD: (30.3nm)  
Min CD: (29.2nm)  
Range: (1.1nm)  
3σ: (0.8nm)

Thicker PR tended to be better LCDU.  
Pillar pattern was collapsed when match thicker PR was used.
Dependence of PR thickness

Hole 30nm / Pitch 60nm, PR-B, F.T.: 40~80nm

EB tool (Elionix), 130kV, 50pA

PR F.T.: 40nm
- Ave. CD: 25.5 nm
- Max CD: 26.8nm
- Min CD: 22.2nm
- Range: 4.6nm
- 3σ: 1.5nm

PR F.T.: 60nm
- Ave. CD: 28.7 nm
- Max CD: 30.2nm
- Min CD: 27.2nm
- Range: 3.0nm
- 3σ: 1.2nm

PR F.T.: 80nm
- Ave. CD: 28.2 nm
- Max CD: 29.5nm
- Min CD: 27.0nm
- Range: 2.5nm
- 3σ: 1.1nm

LCDU became better when thicker pre-pattern was reversed.
Summary of LCDU study

In DDR process, LCDU could be improved by using match thicker PR.
C/H creation with thicker PR

Rev. C/H (PR F.T. : 40nm)

Ave. CD: 28.7nm
Range: 1.9nm
3σ: 1.5nm

Rev. C/H (PR F.T. : 80nm)

Ave. CD: 30.1nm
Range: 1.7nm
3σ: 0.7nm

Original pillar (F.T. : 40nm)
3σ : 0.8nm

Same level!

CDU of Rev. C/H can be improved by using thicker PR.
C/H creation by high sensitive PR

CD size 40nm / Pitch 80nm

<table>
<thead>
<tr>
<th>PR series</th>
<th>Pillar (NTD)</th>
<th>Rev. C/H (NTD-DDR)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PR-B</strong></td>
<td><img src="image1" alt="PR-B Pillar" /></td>
<td><img src="image2" alt="PR-B Rev. C/H" /></td>
</tr>
<tr>
<td>Fujifilm</td>
<td>Dose: 380(\mu)C/cm(^2) Ave. CD: 35.9 nm 3σ: 1.5nm</td>
<td>Dose: 380(\mu)C/cm(^2) Ave. CD: 35.1 nm 3σ: 2.3nm</td>
</tr>
<tr>
<td>Imec STD</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F.T. : 40nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>PR-C</strong></td>
<td><img src="image3" alt="PR-C Pillar" /></td>
<td><img src="image4" alt="PR-C Rev. C/H" /></td>
</tr>
<tr>
<td>Fujifilm</td>
<td>Dose: 200(\mu)C/cm(^2) Ave. CD: 37.7 nm 3σ: 1.4nm</td>
<td>Dose: 200(\mu)C/cm(^2) Ave. CD: 38.7 nm 3σ: 2.0nm</td>
</tr>
<tr>
<td>High sensitivity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F.T. : 40nm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

EB tool (Elionix), 130kV, 50pA

Dose:
- 380\(\mu\)C/cm\(^2\)
- 200\(\mu\)C/cm\(^2\)

Ave. CD:
- 35.9 nm
- 37.7 nm

3σ:
- 1.5nm
- 1.4nm

DDR process showed potential to create fine C/H with high sensitivity.
New DDRM showed low damage property against NTD PR by ToF-SIMS & XPS analysis.

New DDRM with high Si content and high density showed good patterning property in EUV lithography.

Pattern reverse from pillar into C/H was successfully achieved with good LCDU in NTD-DDR process.

LCDU of reversed C/H was improved when thicker PR was applied.

NTD-DDR showed the potential to make fine C/H at match lower dose.

<table>
<thead>
<tr>
<th>Resolution</th>
<th>LWR (CDU)</th>
<th>Sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>HP14nm, A.R. &gt; 2.5!</td>
<td>C30P60, 3σ : 0.7nm! (Same level of original PR)</td>
<td>C40P80 Twice times high sensitivity! compared to STD PR</td>
</tr>
</tbody>
</table>

![EUV](image1.png) ![EUV](image2.png) ![EB](image3.png)
Acknowledgement

Thank you for your kind attention.