EUV Sensitive Si Hard Mask Materials both for PTI & NTI Process

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Electronic Materials Research Lab.
Introduction

• Lithography Technology

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

KrF  ArF  ArF Imm.  DPT  EUV, EB

• Nissan Chemical R&D Activity for EUVL

OBPL (EUV-TC)  EUV-PR  UL

OBPL (OoB Protection Layer)
*10/10 (Thr) The best approach for Outagassing & OoB by EUV TC
*Poster: Feasible solution to control the resist related contamination by TC material

Organic Underlayer (Org. UL)
*Poster: Advances in EUV underlayer toward 1X nm patterning

Inorganic-UL, Main topic in this Presentation
Introduction

RLS trade off

Help minimizing of RLS trade off by Applying functional **Under Layer**.
The requirement of Tri-layer materials

*Tri layer process

FTK: 30-10nm

Inorganic Hard Mask
(Spin coating materials)

O Time, Process & Cost reduction
O Tunable lithography & Etching performance

Si containing Hard Mask (Si-HM)

• Lithography enhancement layer
• Etching hard mask

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Road map for Nissan Si-HM for EUVL

**Minimization of RLS**
- Fast photo speed
- Wide process margin.

**2010**
- 1st gen. Si-HM (NCX7099A)
- For Hp30 nm
- *Fast photospeed*
- *Low outgassing*

**2012**
- 2nd gen. Si-HM (NCX7300)
- For Hp25nm
- *Fast photospeed*

**2013**
- 3rd gen. Si-HM material (NCX7500)
- For Hp20nm
- *Wide PW*
- *Low LWR*
- EUV sensitive unit

**New Target**
- PR & Process universality
  - Methacryl, Hybrid, PHS type PR
  - Positive tone imaging (PTI)
  - Negative tone imaging (NTI)

**New Target**
- Fine pitch pattern etching
  - 20nm L/S pattern transfer

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Target performance of Si-HM

Minimization of RLS
- Fast photo speed
- Wide process margin

EUV Si-HM

2013

3rd gen. Si-HM material
For Hp20nm

EUV sensitive unit

New Target
PR & Process universality
- Methacryl, Hybrid, PHS type PR
- Positive tone imaging (PTI)
- Negative tone imaging (NTD)

New Target
Fine pitch pattern etching
- Dense L/S pattern transfer
- Semi iso Line pattern transfer

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Photo-speed enhancement

EUV sensitive unit

Radical generation unit

EUV chromophore

(High EUV absorption unit: Halogen, Hetero atom)

*The mechanism of acid generation by EUV

EUV Chromophore

RH

MX

X- H+

Acid Generation

RH : Resin
MX : PAG
RH⁺ : Radical cation of resin
R· : Radical of resin
RH(H)⁺ : Protonated resin
M : decomposition of PAG
X⁻ : Counter anion of PAG

ten. Tagawa, Kozawa, et al

EUV sensitive Si-HM

RH°H

RG unit

RG

Ch
### Photo-speed enhancement

**Tool:** MET (Micro Exposure Tool)  
**Condition:** Quadropole (0.68/0.36)  
**PR:** Std. PR

<table>
<thead>
<tr>
<th>Si-HM sample</th>
<th>Std. Si-HM</th>
<th>Radical generation type Si-HM</th>
<th>EUV chromophore type Si-HM</th>
<th>Radical generation &amp; EUV chromophore type Si-HM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top view image</td>
<td></td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>CD (nm)</th>
<th>28.7</th>
<th>30.0</th>
<th>29.2</th>
<th>28.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitivity (mJ/cm²)</td>
<td>13.0 (100%)</td>
<td>10.58 (120%)</td>
<td>10.08 (125%)</td>
<td>9.96 (125%)</td>
</tr>
<tr>
<td>LWR (nm)</td>
<td>6.7</td>
<td>6.4</td>
<td>6.2</td>
<td>5.4</td>
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</tbody>
</table>

Both EUV sensitive unit strongly promotes photo-speed & reduce LWR due to high acid generation.
EUV lithography condition (PTD)

Exposure condition;
NXE:3100
Dipole-60X
NA:0.25 (0.81/0.43)
PR: Hybrid PR (40nm)
UL: Organic UL (20nm) vs Nissan Si-HM (20nm) / SOC (90nm) stack
25nm~ 18nm L/S
Dev. TMAH 2.38% (PTD)
### EUV lithography results @ Hp22nm L/S

<table>
<thead>
<tr>
<th>Stack</th>
<th>Std. Organic UL</th>
<th>Nissan EUV Si-HM / SOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>CD, nm</td>
<td>21.97</td>
<td>22.08</td>
</tr>
<tr>
<td>Dose to size, mJ</td>
<td>12.81</td>
<td>11.74 (+10%)</td>
</tr>
<tr>
<td>LER, nm</td>
<td>3.72 (+7%)</td>
<td>3.99</td>
</tr>
<tr>
<td>DOF at 10% EL, um</td>
<td>0.26</td>
<td>0.28 (+8%)</td>
</tr>
<tr>
<td>Max DOF, um</td>
<td>0.26</td>
<td>0.30 (+13%)</td>
</tr>
<tr>
<td>Max EL, %</td>
<td>20.12</td>
<td>22.54 (+12%)</td>
</tr>
<tr>
<td>Ultimate resolution, nm</td>
<td>Hp20nm</td>
<td>Hp19nm (+5%)</td>
</tr>
</tbody>
</table>

**Top view**

**X-SEM**

**EUV sensitive Si-HM have higher performance in sensitivity, process window & resolution**
EUV lithography results @ fine pitch (Hp1Xnm L/S)

EUV sensitive Si-HM can enhance the resolution hp18~19nm L/S
EUV lithography condition (PTD)

Exposure condition;
NXE:3100
Quasar (Quadropole MP4 45)
NA:0.25 (0.81/0.51)
PR: Hybrid PR (60nm)
UL: Organic UL(20nm) vs Nissan Si-HM (20nm) / SOC (90nm) stack
CH28nm~ CH22nm
Dev. TMAH 2.38% (PTD)
### EUV lithography results @ 26nm C/H (P52nm)

<table>
<thead>
<tr>
<th>Stack</th>
<th>Std. Organic UL</th>
<th>Nissan EUV Si-HM / SOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>CD, nm</td>
<td>26.30</td>
<td>25.72</td>
</tr>
<tr>
<td>Dose to size, mJ</td>
<td>20.98</td>
<td>19.98 (+5%)</td>
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<tr>
<td>1 sigma LCDU</td>
<td>1.20 (+20%)</td>
<td>1.50</td>
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<tr>
<td>Average CER (3 sigma nm)</td>
<td>1.38 (+8%)</td>
<td>1.50</td>
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<tr>
<td>DOF at 10% EL, um</td>
<td>0.24</td>
<td>0.23</td>
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<tr>
<td>Max DOF, um</td>
<td>0.30</td>
<td>0.30</td>
</tr>
<tr>
<td>Max EL, %</td>
<td>13.30</td>
<td>16.57 (+25%)</td>
</tr>
<tr>
<td>Ultimate Resolution, nm</td>
<td>24nm</td>
<td>24nm</td>
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</table>

In C/H patterning, the advantage is sensitivity, process window & PR profile.
Target performance of Si-HM

EUV sensitive Si-HM

Minimization of RLS
- Fast photo speed
- High resolution

PR & Process universality
- Methacryl, Hybrid, PHS type PR
- Positive tone imaging (PTI)
- Negative tone imaging (NTI)

New Target

EUV sensitive unit

2013
3rd gen. Si-HM material
For Hp20nm

New Target

Fine pitch pattern etching
- Dense L/S pattern transfer
- Semi iso Line pattern transfer

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Photo Resist universality

EUV Photo Resist

- **Methacyrl type PR**
- **Hybrid type PR**
- **PHS type PR**

EUV sensitive Si-HM

- No scum,
- No bridge
- No collapse !!!

EUV sensitive Si-HM have high universality with various PR.
Process Universality

Process universality

- **Positive** tone imaging (PTI)
- **Negative** tone imaging (NTI)

*NTI process in EUV lithography

How is the impact of EUV sensitive unit for NTI process??

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Ultimate Resolution of Si-HM for NTI process

<table>
<thead>
<tr>
<th>Si-HM</th>
<th>Sensitivity</th>
<th>40nmLS</th>
<th>35nmLS</th>
<th>32nmLS</th>
<th>30nmLS</th>
<th>28nmLS</th>
<th>26nmLS</th>
<th>25nmLS</th>
<th>24nmLS</th>
<th>23nmLS</th>
<th>22nmLS</th>
<th>21nmLS</th>
<th>20nmLS</th>
<th>19nmLS</th>
<th>18nmLS</th>
<th>17nmLS</th>
<th>16nmLS</th>
<th>15nmLS</th>
<th>14nmLS</th>
<th>13nmLS</th>
<th>12nmLS</th>
<th>11nmLS</th>
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<tbody>
<tr>
<td>Bare-Si (HMDS)</td>
<td>30mJ</td>
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<tr>
<td>EUV chromophore</td>
<td>28mJ (+7%)</td>
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<tr>
<td>Radical generation</td>
<td>29mJ</td>
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<tr>
<td>EUV chromophore &amp; Radical generation</td>
<td>26mJ (+13%)</td>
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</table>

EUV sensitive unit can enhance Resolution, sensitivity and PR adhesion in NTI process

Data Courtesy of EIDEC
Tool: SFET (Small Field Exposure Tool)
Condition: NA=0.3
PR: FFEM

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EUV lithography condition (NTI)

Exposure condition;
MET (Micro Exposure Tool)
Quadropole
NA: 0.3  (0.93/0.36)
PR: Fujifilm PR (50nm)
UL: Nissan Organic UL (5nm) vs Si-HM (20nm) / SOC (90nm) stack
26nm~ 22nm L/S
Dev. Organic Solvent (NTD)
**EUV lithography results @ 24nm L/S in NTI process**

<table>
<thead>
<tr>
<th>Stack</th>
<th>Nissan Organic UL (for NTI)</th>
<th>Nissan EUV Si-HM / SOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>CD, nm</td>
<td>24.5</td>
<td>24.2</td>
</tr>
<tr>
<td>Dose, mJ</td>
<td>21.0</td>
<td>22.0</td>
</tr>
<tr>
<td>LWR, nm</td>
<td>4.6</td>
<td>3.9 (+15%)</td>
</tr>
<tr>
<td>DOF, nm</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>10 %EL, %</td>
<td>16.8</td>
<td>20.6 (+23%)</td>
</tr>
</tbody>
</table>

Ultimate Resolution, nm

- **Top view**
- **X-SEM**

EUV Si-HM can enhance LWR & Process Window in NTI process.

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EUV Si-HM could enhance the resolution to 22nm L/S in NTI process by applying EUV sensitive unit.

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Target performance of Si-HM

Material Design for EUVL

Minimization of RLS
- Fast photo speed
- High resolution

2013

EUV sensitive unit

3rd gen. Si-HM material

For Hp20nm

PR & Process universality
- Positive tone process (PTI)
- Negative tone process (NTI)

New Target

Fine pattern etching
- 20nm L/S pattern transfer

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Etching demonstration~Hp30nm dense L/S~

L/S: 30nm / 30nm

Si-HM open: CF₄ and others
SOC open: O₂ and others

EUV-sensitive Si containing Hard Mask (Si-HM) for PTD and NTD process in EUVL
Wataru Shibayama, Nissan Chemical

Our EUV Si-HM have enough etching resistance at fine pitch.

Hp 20nm dense L/S Pattern etching

Our EUV Si-HM have enough etching selectivity even in 10nm FTK at 20nm line

NISSAN CHEMICAL INDUSTRIES, LTD. Electronic Materials Research Laboratories.
Etching demonstration ~Hp20nm dense L/S~

Our EUV Si-HM have enough etching resistance at hp 20nm.

NISSAN CHEMICAL INDUSTRIES, LTD. Electronic Materials Research Laboratories.
Target performance of Si-HM

Material Design for EUVL

Minimization of RLS
- Fast photo speed
- Wide process margin

3rd gen. Si-HM material (NCX7500)
For Hp20nm

2013

EUV sensitive unit

PR & Process universality
- Methacryl, Hybrid, PHS type PR
- Positive tone imaging (PTI)
- Negative tone imaging (NTI)

New Target

Fine pattern etching
- 20nm L/S pattern transfer

NISSAN CHEMICAL INDUSTRIES, LTD. Electronic Materials Research Laboratories.
New Nissan EUV Si-HM for **PTI & NTI** : NCX7500

**NCX7500**

*Base polymer*

Radical generation & **EUV chromophore**

- High sensitivity, low LWR & wide PW in PTI
- High sensitivity, wide PW & High resolution in NTI

**NCX7500 has high universality for PTI & NTI with any PR around hp 20nm**

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Summary

• Novel Si-HM with EUV sensitive unit has been developed.

• Radical generation unit, EUV chromophore can improve sensitivity, LWR and Process window

• In PTI process, Hp19nm L/S pattern can be achieved by applying EUV Sensitive Si-HM

• 20nm dense L/S pattern can be transferred to SOC layer successfully

• Nissan EUV sensitive Si-HM have wide universality with several type PR in both PTI & NTI process
Acknowledgement

Thank you for kind attention