Development of NIL-Template dry-cleaning process
- VUV cleaning technology -

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Particle adsorption onto NIL-Template by Gas-phase organics excited during VUV cleaning
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  • Nano-Imprint Lithography (NIL) applications
  • Resist residue and its removal on NIL template
  • Vacuum Ultraviolet (VUV) cleaning performance

➢ Experiments and Results
  • Analysis of VUV damage and Particle on NIL template
  • Analysis of Organic contamination on NIL template
  • Model of particle adsorption on NIL template

➢ Summary
## Conventional lithography vs. NIL on Memory Device

<table>
<thead>
<tr>
<th></th>
<th>Conventional lithography</th>
<th>Nano imprint lithography (NIL)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cost</strong></td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td><strong>Process</strong></td>
<td>Non-contact</td>
<td>Contact</td>
</tr>
<tr>
<td><strong>Cleaning margin</strong></td>
<td>Wide (Qz mask)</td>
<td>Narrow (Qz template)</td>
</tr>
</tbody>
</table>

### Conventional lithography:
- **Light source**
- **Condenser lens**
- **Photo mask (Qz)**
- **Projection lens**
- **Wafer**

### Nano imprint lithography (NIL):
- **Dispense resist:**
  - **Template (Qz)**
  - **Resist dispenser**
- **Align & Imprint:**
  - **Underlayer**
  - **Si wafer sub.**
- **Expose UV:**
- **Separate template:**
  - **Remaining layer**
The cleaning margin on NIL template is getting much narrower due to contact process as well as smaller pattern size.
Various applications on NIL

Characteristics of NIL
- Direct Pattern Transfer
- High Resolution

Hp1x-nm line;

Diagonal line;

2x-nm hole;

Pillar;
Resist residue & cleaning on NIL template

- Template cleaning:
  - Resist residue on template
  - Resist removal by VUV:

- NIL:
  - Template
  - Resist
  - RIE:

- Wafer process:
  - Incoming wafers
  - Missing pattern
  - Resist remove:
  - Post RIE processes

Resist residue happens on the template. It should be removed.
# Cleaning processes for NIL template

<table>
<thead>
<tr>
<th>Process step:</th>
<th>Removal material:</th>
<th>Throughput (a.u.):</th>
<th>Concerns:</th>
</tr>
</thead>
<tbody>
<tr>
<td>APM (Wet) NH₄OH:H₂O₂</td>
<td>Inorganic</td>
<td>1.0</td>
<td>Pattern damage</td>
</tr>
<tr>
<td>SPM (Wet) H₂SO₄:H₂O₂</td>
<td>Organics</td>
<td>1.0</td>
<td>Sulfur residue</td>
</tr>
<tr>
<td>SPM/AMP (Wet)</td>
<td>Organics/Inorganic</td>
<td>0.5</td>
<td>Pattern damage, Low throughput</td>
</tr>
<tr>
<td>DIO₃ (Wet)</td>
<td>Organics</td>
<td>1.5</td>
<td>Poor removability</td>
</tr>
<tr>
<td>O₂- Asher (Dry)</td>
<td>Organics</td>
<td>3.0</td>
<td>Metal mark damage</td>
</tr>
<tr>
<td>VUV-O₃ (Dry)</td>
<td>Organics</td>
<td>2.5</td>
<td>Metal mark damage?</td>
</tr>
</tbody>
</table>

SPM/APM clean is current process (throughput: 0.5)

How does VUV remove organics (e.g. resist, carbon contamination)?
Photochemical reaction on VUV cleaning

Components of organics:

<table>
<thead>
<tr>
<th>Components</th>
<th>Binding energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C</td>
<td>84</td>
</tr>
<tr>
<td>C=C</td>
<td>141</td>
</tr>
<tr>
<td>C-H</td>
<td>98</td>
</tr>
<tr>
<td>C-F</td>
<td>115</td>
</tr>
<tr>
<td>C-N</td>
<td>64</td>
</tr>
<tr>
<td>C-O</td>
<td>76</td>
</tr>
<tr>
<td>C=O</td>
<td>190</td>
</tr>
<tr>
<td>O-O</td>
<td>118</td>
</tr>
<tr>
<td>O-H</td>
<td>109</td>
</tr>
<tr>
<td>Si-O</td>
<td>105</td>
</tr>
<tr>
<td>Si-C</td>
<td>70</td>
</tr>
</tbody>
</table>

Organics are removed as followings:

\[ \text{O}_2 \text{ (in Air)} + \text{VUV} \text{ hv (172nm)} \rightarrow \text{O}^* + \text{O} \text{ (3P)} \]

\[ \text{O} \text{ (3P)} + \text{O}_2 \rightarrow \text{O}_3 \]

\[ \text{O}_3 + \text{hv (172nm)} \rightarrow \text{O}^* + \text{O}_2 \]

Organics: \[ C_mH_nO_k + \text{hv (172nm)} \rightarrow C_{m'}H_{n'}O_{k'} \]

\[ C_{m'}H_{n'}O_{k'} + \text{O}^* \rightarrow \text{H}_2\text{O}, \text{CO}, \text{CO}_2, C_mH_n \uparrow \text{ (Gas)} \]

\[ \text{O}^* : \text{Active oxygen [Radical]} \]

\[ \text{O (3P): Ground state oxygen} \]

Basic removal performance on VUV cleaning

- Resist film removal:
  - VUV Power: 80mW/cm²
  - Removal rate: 50nm/min
  - VUV 5min gives perfect removal

- XPS analysis:
  - VUV irradiation time:
    - 4 min
    - 5 min
    - BG: background
  - Signal intensity (a.u.)
  - Binding energy (eV)

- Residual resist removal:
  - Residual resist on template with imprinting of several lots

VUV clean perfectly removes resist. How about VUV damage?
# Test template on VUV damage evaluation

<table>
<thead>
<tr>
<th>Side view:</th>
<th>Actual template:</th>
<th>Test template (NO pattern):</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal alignment mark</td>
<td>Metal film</td>
<td>Whole coated metal film</td>
</tr>
<tr>
<td>Mesa (pattern region)</td>
<td>quartz</td>
<td>Metal film</td>
</tr>
</tbody>
</table>

**Top view:**
- VUV irradiation region
- NO VUV region

Border line between NO VUV and VUV region.

Test template wholly coated with metal film is evaluated.
Evaluation flow: VUV damage & Chamber cleanliness

■ Evaluation flow:

1st
without VUV

2nd
With VUV

- Load template in VUV chamber
- Wait for several hours
- Turn on VUV
  1. Analyze particle on template
  2. Analyze organics by GC-MS
  3. Analyze organic/inorganic by TOF-SIMS

■ VUV irradiation:

- Both templates are placed in SIMF during transportation.
- VUV is turned off for 5 days before loading the both templates.
- But, only 2nd template is irradiated with VUV.
Particles generated at VUV region and also near the border line.
Since there is no difference at both regions on metal signal, it is concluded that VUV does not damage metal film.

However, Hydrocarbon ($C_xH_y^+$) increased on VUV region where particles generated.
Result: Si+ and SiO$_3^-$ Signal on VUV region

- TOF-SIMS -

Turn off: 5 days

➢ TOF-SIMS also detected Si+ and SiO$_3^-$ at the VUV region.
Results: VUV turn off term vs. Particle increase

- Particles increased with increasing VUV turn off term.
- Organics could be accumulated in the chamber with off term.

Graph:
- X-axis: VUV turn off term (days)
- Y-axis: Particle after VUV (a.u.)

With VUV
- Irradiation time: 10 min constant
- Turn off: 5 days
- 1 day OK
Results: GC-MS analysis on whole template region

Turn off: 5 days

- without VUV, TOC: 310 ng
- with VUV, TOC: 110 ng

But particles were generated at VUV region.

C<sub>x</sub>H<sub>y</sub> and Organosiloxane were found on the whole template without VUV.

These organics were dramatically decreased by VUV irradiation (one third), however particles were generated at VUV irradiation region.

Organics (Aliphatic):

<table>
<thead>
<tr>
<th>Material</th>
<th>Weight [g/mol]</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 1-Dodecene</td>
<td>168</td>
<td>C&lt;sub&gt;10&lt;/sub&gt;H&lt;sub&gt;21&lt;/sub&gt;CH=CH&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>B 7-tetradecene</td>
<td>196</td>
<td>C&lt;sub&gt;14&lt;/sub&gt;H&lt;sub&gt;28&lt;/sub&gt;</td>
</tr>
<tr>
<td>C Cyclopentadecanone</td>
<td>210</td>
<td>C&lt;sub&gt;15&lt;/sub&gt;H&lt;sub&gt;30&lt;/sub&gt;</td>
</tr>
<tr>
<td>D Octadecane</td>
<td>254</td>
<td>C&lt;sub&gt;18&lt;/sub&gt;H&lt;sub&gt;38&lt;/sub&gt;</td>
</tr>
<tr>
<td>E Heneicosane</td>
<td>290</td>
<td>C&lt;sub&gt;21&lt;/sub&gt;H&lt;sub&gt;44&lt;/sub&gt;</td>
</tr>
<tr>
<td>F Organosiloxane</td>
<td>296</td>
<td>4[(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;SiO]</td>
</tr>
</tbody>
</table>

Structure:

A: \[\cdots\cdots\cdots\cdots\cdots\cdots\cdots\]  C: \[
B: \[\cdots\cdots\cdots\cdots\cdots\cdots\cdots\]  D: \[
E: \[\cdots\cdots\cdots\cdots\cdots\cdots\cdots\]
Results: - Organosiloxane - GC-MS analysis

Turn off: 5 days

<table>
<thead>
<tr>
<th>Without VUV</th>
<th>With VUV</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Signal intensity without VUV" /></td>
<td><img src="image2.png" alt="Signal intensity with VUV" /></td>
</tr>
</tbody>
</table>

Retention time (min)

Signal intensity (a.u.)

Mas Spectrum on OMCTS

Sample data

Actual data: matching 98% to OMCTS Octa-Metchel- Cycric-Tetra-Sliroxan.
Organic gases are accumulated in the chamber.

Concentration of the Organic gases goes over the threshold.

Most organic gases are activated by VUV on the irradiation region.

Active-organics condense each other, then grow as particles on both gas phase and template surface. Most organics condensed by VUV could be exhausted out of chamber, according to GC-MS analysis.

It is important to manage the turn off term how long not over the threshold of the organic gases’ concentration.
Chemical reaction related to SiO$_2$ particle generation:

**Generation of radicals:**

\[ \text{O}_2 + \text{VUV h}_\nu (172\text{nm}) \rightarrow \text{O}^* + \text{O} (^{3}\text{P}) \]
\[ \text{O} (^{3}\text{P}) + \text{O}_2 \rightarrow \text{O}_3, \text{O}_3 + \text{h}_\nu \rightarrow \text{O}^* + \text{O}_2 \]
\[ \text{H}_2\text{O} + \text{VUV h}_\nu (172\text{nm}) \rightarrow ^*\text{OH} + \text{H}^* \]

VUV activates and/or degrades OMCTS.

**Overall reaction 1:**

Oxygen radicals oxidize OMCTS.

\[ 4[\text{SiO}_2(\text{CH}_3')_2] + 4\text{O}^* \rightarrow 4\text{SiO}_2 + 4\text{C}_2\text{H}_6 \uparrow (\text{Ethane gas}) \]

**Overall reaction 2:**

Hydroxyl and Hydride radicals react OMCTS.

\[ 4[\text{SiO}_2(\text{CH}_3')_2] + 4 (^*\text{OH}, \text{H}^*) \rightarrow 4\text{SiO}_2 + 8\text{CH}_4 \uparrow (\text{Methane gas}) \]
Summary

- **VUV clean technology has been developed on NIL-template.**
  - TOF-SIMS showed VUV did not damage metal film on the template.
  - Throughput of NIL-template clean improved by VUV cleaning.

- **However, TOF-SIMS detected C_mH_n and SiO at the VUV region,**
  even though VUV decreased C_mH_n and organosilane on the template.
  - Cluster particles were also found at the VUV region.
  - Particles increased with increasing VUV turn-off term.

- **Model of particle generation is proposed:**
  1\textsuperscript{st} step, organic gases are accumulated into the VUV chamber,
  2\textsuperscript{nd} step, the organics, O\textsubscript{2}, and H\textsubscript{2}O gases are activated by VUV.
  3\textsuperscript{rd} step, the active gases condense each other, then grow as particles

- **Solution of particle generation is proposed:**
  - Managing the turn off term on VUV irradiation.
  - VUV irradiation on the appropriate timing.
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