Development Status of EUVL Blank and Substrate

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Toshiyuki Uno
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1. Introduction
EUVL mask blank has a stack of reflective, capping, absorber and antireflective layers on its front side for a patterning and a conductive layer on its back side for mask chucking.

**Structure of EUV mask blank**

- Resist film
- Antireflective layer
- Absorber layer
- Capping (and/or Buffer) layer
- Reflective multilayer
- Glass substrate
- Conductive layer for electrostatic chuck
AGC is taking care of all processes essential to EUV mask blank: LTEM material, polishing, cleaning, film deposition and resist coat.

1-2 EUVL mask blank manufacturing process

- **Material synthesis**: Flame hydrolysis of Si and Ti source materials to form the Ti-doped SiO$_2$ glass ingot
- **Slicing**: Slice the glass ingots into 6025 plates
- **Lapping & Polishing**: Lap and polish to smooth & flat surfaces
- **Cleaning**: Remove particles and polishing slurries
- **Film deposition**: Deposit reflective, capping, absorber and ARC films
- **Resist coat**
AGC possesses critical metrology tool sets, which make it possible to realize the total quality improvement of blanks.

<table>
<thead>
<tr>
<th>Metrology tools</th>
<th>Pilot line</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTE measurement</td>
<td>Dilatometer (ASET model)</td>
</tr>
<tr>
<td>Defect inspection</td>
<td>Lasertec M1350A</td>
</tr>
<tr>
<td>Defect analysis</td>
<td>SEM/EDS</td>
</tr>
<tr>
<td>Surface flatness</td>
<td>Interferometer</td>
</tr>
<tr>
<td>Surface roughness</td>
<td>AFM</td>
</tr>
<tr>
<td></td>
<td>Zygo Newview</td>
</tr>
<tr>
<td>EUV reflectometer</td>
<td>Stand Alone</td>
</tr>
<tr>
<td>DUV~NIR reflectometer</td>
<td>Hitachi, Shimadzu</td>
</tr>
</tbody>
</table>

In addition to these, we also have various kinds of defect characterization tools (u-FTIR, u-Raman,…), film characterization tools (XRR, XRD,…) and dry etcher.
2. Blank defect reduction
2-1 Inspection and size of native defects

- The real size of defect increases with the relative defect size (pixel) provided by the defect inspection tool (M1350A).
- Pixel 3 corresponds to 34nm SEVD (Sphere equivalent volume diameter), Pixel 8 to 56nm SEVD.

**M1350A pixel vs real defect size**

- **Depth or Height**
- **SEVD**
- **Full width**

Typical defect map and histogram of M1350A inspection

Native defect → Volume by AFM → Equiv. Sphere
We have been optimizing the polishing conditions by changing processes parameters, conditioning and materials to reduce the substrate pit.

The results shown here were ML pit count & relative yield ($10Q1-2 = 100$) of QZ test plates. We demonstrated 0 pit @56nm SEVD (sphere equiv. volume diameter).

**ML Pit defect count trend**

<table>
<thead>
<tr>
<th></th>
<th>08Q4</th>
<th>09Q1</th>
<th>09Q3</th>
<th>10Q1-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>ML pit count</td>
<td>16</td>
<td>8</td>
<td>9</td>
<td>7</td>
</tr>
<tr>
<td>Best pit count</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Best pit count @ 56nm SEVD</td>
<td>20</td>
<td>10</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>Best pit count @ 34nm SEVD</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

**ML Pit defect yield trend**

<table>
<thead>
<tr>
<th></th>
<th>08Q4</th>
<th>09Q1</th>
<th>09Q3</th>
<th>10Q1-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative Yield</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>0 pit yield @ 56nm SEVD</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>&lt;=15 pit yield @ 34nm SEVD</td>
<td>47</td>
<td>48</td>
<td>64</td>
<td>100</td>
</tr>
</tbody>
</table>
The average defects counts on LTEM substrates @ p1+ and relative yield of 0 unremoval particle were shown below.

To reduce un-removal particles, we installed the new intermediate cleaning tool in 09Q3. Consequently, the number of un-removal particles on LTEM substrate has been drastically decreased.

We expect that “added particle” will be decreased further by optimizing the final cleaning processes.

![Graph showing average defect counts of LTEM substrates](image)
This is the best defect trend of the LTEM-ML blank where the substrate flatness is <150mm.
We have improved the absorber adder defect performance.

- The adder defect count has been decreased by optimizing coating equipment.
- We have obtained several plates with no adder defect larger than 100nm SEVD.
3. Integrated & Best performances
3-1 Integrated performance of LTEM-ML blank

Structure
CrN/LTEM/ML/Ru

CTE of LTEM
Mean CTE -3.5 ppb/K
CTE variation (PV) 1.7 ppb/K

Substrate flatness
front 89 nm
back 76 nm
Blank Flatness (Bow) 0.38 um

Reflectivity
Peak R 66.2 %
R range (Abs.) 0.3 %
centroid λ 13.535 nm
λ range 0.026 nm

Defect map and histogram

Pixel Histogram

0.05 cm$^{-2}$ @ >56nm SEVD
0.12 cm$^{-2}$ @ >34nm SEVD
### 3-2 Best performance of LTEM - ML Blank

We can mostly achieve the requirements other than defect.

<table>
<thead>
<tr>
<th>Requirements (SEMI P37,38)</th>
<th>current</th>
<th>best</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Substrate</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CTE mean</td>
<td>+/-5 ppb/K</td>
<td>0 ppb/K</td>
</tr>
<tr>
<td>CTE variation</td>
<td>+/-3 ppb/K</td>
<td>+/-1 ppb/K</td>
</tr>
<tr>
<td>flatness (front)</td>
<td>&lt;30 nm</td>
<td>38 nm on LTEM</td>
</tr>
<tr>
<td>flatness (back)</td>
<td>&lt;30 nm</td>
<td>48 nm on LTEM</td>
</tr>
<tr>
<td>HSFR (RMS)</td>
<td>&lt;0.15 nm</td>
<td></td>
</tr>
<tr>
<td><strong>ML/Capping</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Defect (ML/Cap)</td>
<td>0.00 c/cm² @30 nm</td>
<td>0.04@56nm (SEVD)</td>
</tr>
<tr>
<td>Peak Reflectivity</td>
<td>&gt;67 %</td>
<td>67.1</td>
</tr>
<tr>
<td>Mean Centroid λ</td>
<td>n/a</td>
<td>0 to target</td>
</tr>
<tr>
<td>FWHM</td>
<td>&gt;0.50 nm</td>
<td>&gt;0.50 nm</td>
</tr>
</tbody>
</table>

**Color Code**
- Green: met SEMI spec.
- yellow: TBD
- Red: need development
4-1. New capping film

AGC has developed the new Ru film, which showed better chemical & thermal durabilities than the conventional (current) Ru film.
4-1-1 EUV reflectivity change upon O3-DIW cleaning

- The new Ru capped ML showed the better durability upon the wet cleaning using ozonated water (~30ppm) than the conventional Ru (2.5nm).
- In the new Ru capped ML blank, the reflectivity drop was <1% and the reflectivity after cleaning was >65%. This effect of the new Ru has been confirmed repeatedly.

Fig. EUV reflectivity spectrum before and after O3-DIW cleaning (~30ppm x 10min)
No clear difference of roughness was observed in both new Ru and conventional Ru films.

Fig. Surface roughness of QZ/ML/Ru

**New Ru (~2.5nm)**

- As-depo: Rms=0.94nm
- Post-Cleaning: Rms=0.82nm

**Conventional Ru (~2.5nm)**

- As-depo: Rms=1.02nm
- Post-Cleaning: Rms=0.99nm
4-1-3 EUV reflectivity change upon thermal treatment

The new Ru film also showed the better thermal durability in air than the conventional Ru film.

Fig. EUV reflectivity spectrum before and after the thermal annealing (210°Cx10min, in air)
4-2 193nm ARC
4-2-1  193nm ARC candidate material

AGC released the blanks with 2 types of New ARC layers for 193nm mask inspection.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Standard</th>
<th>Candidate 1</th>
<th>Candidate 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TaON ARC 7nm</td>
<td>ARC-1 8nm</td>
<td>ARC-2 12nm</td>
</tr>
<tr>
<td></td>
<td>TaN Absorber</td>
<td>TaN Absorber</td>
<td>TaN Absorber</td>
</tr>
<tr>
<td></td>
<td>Ru</td>
<td>Ru</td>
<td>Ru</td>
</tr>
<tr>
<td></td>
<td>ML</td>
<td>ML</td>
<td>ML</td>
</tr>
<tr>
<td>R%@193nm</td>
<td>&gt; 20%</td>
<td>&lt; 7%</td>
<td>&lt; 7%</td>
</tr>
<tr>
<td>Feature</td>
<td>ARC for 257nm</td>
<td>Thinner ARC Lower Etching Rate</td>
<td>Thicker ARC Higher Etching Rate</td>
</tr>
</tbody>
</table>
This is the measurement result of DUV spectra of TaN(51nm)/ARC-1(6~10nm).
The samples more than 8nm thickness shown here had <7% reflectivity at 193nm.
4-2-3 Candidate 2 ~DUV performances~

- This is the measurement result of DUV spectra of TaN(51nm)/ARC-2(11~13nm).
- All three samples shown here had <7% reflectivity at 193nm.
- Absorber with ARC-2 can be etched by one-step with Cl2 chemical.

Fig. DUV reflectivity spectra

Reflectivity (%) vs. wavelength (nm)

- TaN(51nm)/ARC-2 (11nm)
- TaN(51nm)/ARC-2 (12nm)
- TaN(51nm)/ARC-2 (13nm)

Reflectivity at 193nm: <7%
Reflectivity at 257nm: ~20%
Durability performances for 60min were investigated.
Both materials candidates showed no degradation upon H2SO4, SC1 and 150°C thermal annealing for 60min.

Fig. Durability performances: DUV bottom reflectivity changes

Durability Test Condition
SC1: 40°C 60min Dip
H2SO4(98%): 40°C 60min Dip
Heat: 150°C 60min in Air
5. Roadmap of EUVL Blank development
AGC is carrying out the process development of 1\textsuperscript{st} generation blank. AGC is also developing the material of 2\textsuperscript{nd} generation blank which will be suitable for 16nm hp and off-axis illumination.

<table>
<thead>
<tr>
<th>Generation</th>
<th>Substrate</th>
<th>Capping</th>
<th>Absorber</th>
<th>ARC</th>
</tr>
</thead>
<tbody>
<tr>
<td>1\textsuperscript{st}</td>
<td>LTEM w/zero CTE@22oC (Flatness&lt;100nm)</td>
<td>Ru or New Ru</td>
<td>TaN (51nm or 77nm)</td>
<td>TaON or 193nm ARC</td>
</tr>
<tr>
<td>2\textsuperscript{nd}</td>
<td>LTEM w/ zero CTE @ high temperature?</td>
<td>New Ru</td>
<td>New material (30~40nm)</td>
<td>TaON or 193nm ARC or no ARC</td>
</tr>
</tbody>
</table>

**Table:**

<table>
<thead>
<tr>
<th>Year</th>
<th>2009</th>
<th>2010</th>
<th>2011</th>
<th>2012</th>
<th>2013</th>
<th>2014</th>
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<tbody>
<tr>
<td>H1</td>
<td></td>
<td>H1</td>
<td></td>
<td>H1</td>
<td></td>
<td>H1</td>
</tr>
<tr>
<td>H2</td>
<td></td>
<td></td>
<td>H2</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Diagram:**

- **1\textsuperscript{st} generation**
  - Process development at Pilot line
  - HVM

- **2\textsuperscript{nd} generation**
  - Material development
  - Process development
  - HVM

*Any needs for LTEM w/ zero CTE at elevated temperature?*
The tool upgrade and improvement of polishing and intermediate cleaning were carried out, which resulted in the significant improvement of substrate defect performance and yield.

Continuous improvement and integration are in progress at AGC and single defect counts on ML blank @ 54nm SEVD has been achieved.

AGC successfully introduced New-Ru capping film and 193nm ARC to the industry.