Etching Properties and Optical Emission Spectroscopy of NH$_3$ Added C$_5$F$_8$ Pulse-Modulated ICP Plasma

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Etching Mechanism for CW Plasma

- High electron temperature
- High amount of F radical
- Thin protection film
- Si etching takes place by the fluorine atoms.

Low selectivity (SiO$_2$/Si)

Etching Mechanism for Pulse-Modulated Plasma

- Low electron temperature
- Reduced F radical
- Thick protection film
- High selectivity (SiO$_2$/Si)

Etching Shape Comparison with Hole Size

Gas: c-C$_5$F$_8$:O$_2$:Ar=11:4:60 (sccm)
ON/OFF time = 25/25 (usec)

Shape of the hole depends on the hole size. The number of additional ions, which are reflected from the sidewall and reach the bottom surface of the hole, becomes small for the small hole size.
**Electron Temperature Measurement by Langmuir Probe**

Comparison of electron temperature between CW ICP and pulse-modulated ICP:
- Electron temperature decreases by pulse modulation.
- Pulse modulation is expected to improve etching selectivity.

**Effect of Pulse-Modulated Plasma**

- Electron temperature decreases by pulse modulation.
- Pulse modulation is expected to improve etching selectivity, but we couldn’t get the required selectivity.
- Improvement by pulse modulation is limited.

**NH₃ Addition**

- High molecule polymer radical increases large adsorption probability.
- Taper angle and selectivity trade off.

- Reduce protection film thickness (Ion bombardment and chemical etching).
- Oxygen adding reduces selectivity.
- NH₃ is replaced with oxygen.
- Selectivity improved.

**SEM of Contact Hole etched with NH₃**

- NH₃ added (2sccm).
- Selectivity(SiO₂/Si)≈80.
- High aspect ratio (＞10).
Comparison of Adding Gas (H\textsubscript{2}, NH\textsubscript{3})

Etchstop is suppressed by NH\textsubscript{3} addition instead of H\textsubscript{2}.

- NH\textsubscript{3} addition: NH + 2H → large etch rate
- H\textsubscript{2} addition: 2H → small etch rate

C\textsubscript{5}F\textsubscript{8}/Ar/X = 11/60/2 (sccm)

<table>
<thead>
<tr>
<th>Addition Gas</th>
<th>Etching depth (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H\textsubscript{2}</td>
<td>500</td>
</tr>
<tr>
<td>NH\textsubscript{3}</td>
<td>1000</td>
</tr>
</tbody>
</table>

Bottom | Surface

Comparison of Adding Gas (O\textsubscript{2}, NH\textsubscript{3})

Selectivity is decreased by O\textsubscript{2} addition.

C\textsubscript{5}F\textsubscript{8}/Ar/X = 11/60/2 (sccm)

<table>
<thead>
<tr>
<th>Addition Gas</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>O\textsubscript{2} added</td>
<td>50</td>
</tr>
<tr>
<td>NH\textsubscript{3} added</td>
<td>0</td>
</tr>
</tbody>
</table>

Optical Emission Spectroscopy (OES)

H is increasing. Etching of polymers takes place.
Vertical sidewall is obtained.

OES Intensity vs H\textsubscript{2} Flow Rate

H\textsubscript{2} = 2 sccm | H\textsubscript{2} = 0 sccm
Comparison of Adding Gas ($H_2$)

<table>
<thead>
<tr>
<th>$H_2$</th>
<th>$Selectivity (SiO_2/ Si)$</th>
<th>Etching Rate (nm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 sccm</td>
<td>500</td>
<td>200</td>
</tr>
<tr>
<td>2 sccm</td>
<td>300</td>
<td>100</td>
</tr>
</tbody>
</table>

Center of large pattern

SiO$_2$ etching rate has maximum at $NH_3=1$ sccm.

OES Intensity vs $NH_3$ Flow Rate

CN (precursor of HCN, FCN) is increasing. HCN and FCN are volatile. Deposition film thickness is reduced. Contact hole etching with vertical sidewall is obtained.

Influence of plasma without reflective ion from sidewall is investigated.

SiO$_2$ etching rate curve has a peak.

The reason of SiO$_2$ etching rate
Conclusions
1. Excellent etching properties are achieved with following condition
   • Pulse-modulated plasma improves SiO₂/Si selectivity, due to the lowering of electron temperature.
   • C₅F₈/Ar added with NH₃ → High aspect ratio (>10)
     Good selectivity (SiO₂/Si≥80)

2. Optical Emission Spectroscopy measurement revealed that
   • CN and NH are generated by NH₃ addition.
   • OES result has good correlation with SiO₂ etching rate.

3. CN compound (ex. HCN, FCN) may reduce CₓFᵧ polymer, and NH (with CₓFᵧ) may cause CₓNᵧ polymer.
   Etchstop and selectivity can be controlled by NH₃ addition.