Experiments and Modeling of Mass Transfer for Cross-Contamination in Plasma Processes

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Thrust B: Subtask B5-3

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Outline

• Background on issues
• Motivation
• Cross-contamination experiments
  - Procedure and results
• Mass transfer model
  - Comparison to experimental results
  - Transfer coefficients, k
• Other contaminants
• Conclusions and future applications
Background

- Material diversity increases as process complexity increases

After Peercy, P.S, IEEE1998
Background (2)

- Issues of cross-contamination
  - Low volatility material is hard to remove from chamber
  - New materials may require their own dedicated chamber
  - Mass transfer mechanism between chamber wall and wafer needs to be understood

![Vollatility of Metal Chlorides](image)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlCl3</td>
<td></td>
</tr>
<tr>
<td>BCl3</td>
<td></td>
</tr>
<tr>
<td>CuCl</td>
<td></td>
</tr>
<tr>
<td>Cl2</td>
<td></td>
</tr>
<tr>
<td>FeCl2</td>
<td></td>
</tr>
<tr>
<td>FeCl3</td>
<td></td>
</tr>
<tr>
<td>HfCl4</td>
<td></td>
</tr>
<tr>
<td>MgCl2</td>
<td></td>
</tr>
<tr>
<td>NiCl2</td>
<td></td>
</tr>
<tr>
<td>SiCl4</td>
<td></td>
</tr>
<tr>
<td>TiCl4</td>
<td></td>
</tr>
<tr>
<td>TaCl5</td>
<td></td>
</tr>
<tr>
<td>ZrCl4</td>
<td></td>
</tr>
</tbody>
</table>
Motivation for Studying Zr Contamination Rate Transfer

- ZrO$_2$ is a promising candidate for gate dielectric
- Calculations suggest that interstitial Zr and Hf have mid-gap trap levels
- Interstitial Zr and Hf are expected to have high diffusion rates in Si
- ZrO$_2$ etch by-products are less volatile than SiO$_2$ etch by-products
- Good vehicle for studying contamination rate transfer
Motivation for Studying Zr Contamination Rate Transfer (2)

ESH:

• Understanding mass transfer can help optimize chamber cleaning, wafer cleaning

• Know how long chamber needs to be seasoned to reduce cross-contamination

• Help choose cleaning scheme to increase yields and reliability
Experimental Setup

- Applied Materials P5000 MERIE plasma etcher
- Measure contamination on wafers following ZrO₂ etching
- Use TOF-SIMS (collaborated with Physical Electronics, Inc.)
  - detection limit $\sim 7 \times 10^7$ atoms/cm² for Zr
Experimental Setup (2)

Accumulation

- **SiO$_2$**
- **SiO$_2$**
- **ZrO$_2$**
- **SiO$_2$**
- **ZrO$_2$**
- **SiO$_2$**

Process Time

- Baseline for chamber
- Sample contamination accumulation
- Sample contamination accumulation

Decay

- **ZrO$_2$**
- **SiO$_2$**
- **SiO$_2$**
- **SiO$_2$**

Process Time

- Contamination accumulation in chamber
- Sample contamination decay
- Contamination accumulation in chamber
Experiment 1 Results

Accumulation

Process Time

Decay

- Non-linear accumulation
- Two decay stages

Wet Clean

S1 SiO₂

360s seasoning

S2 SiO₂

60s

Z1 ZrO₂

30s

S3 SiO₂

30s

Z2 ZrO₂

30s

S4 SiO₂

30s

Z3 ZrO₂

30s

S5 SiO₂

30s

Z4 ZrO₂

30s

S6 SiO₂

30s

Z5 ZrO₂

120s

S7 SiO₂

15s

S8 SiO₂

30s

S9 SiO₂

180s

S10 SiO₂

360s seasoning

S11 SiO₂

180s

Accumulation

Decay

Z Contamination (#/cm²)

Net Process Time (s)
Experiment 2 Results

Accumulation
- Correlates well with expt.1
- Non-linear accumulation
- Two decay stages

Decay

<table>
<thead>
<tr>
<th>Process Time</th>
<th>Accumulation</th>
<th>Net Process Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>360s</td>
<td>S1 SiO₂</td>
<td>0</td>
</tr>
<tr>
<td>60s</td>
<td>S2 SiO₂</td>
<td></td>
</tr>
<tr>
<td>30s</td>
<td>Z1 ZrO₂</td>
<td></td>
</tr>
<tr>
<td>30s</td>
<td>Z2 SiO₂</td>
<td></td>
</tr>
<tr>
<td>30s</td>
<td>Z3 ZrO₂</td>
<td></td>
</tr>
<tr>
<td>30s</td>
<td>Z4 SiO₂</td>
<td></td>
</tr>
<tr>
<td>30s</td>
<td>Z5 ZrO₂</td>
<td></td>
</tr>
<tr>
<td>30s</td>
<td>Z6 SiO₂</td>
<td></td>
</tr>
<tr>
<td>30s</td>
<td>Z7 ZrO₂</td>
<td></td>
</tr>
<tr>
<td>120s</td>
<td>S8 SiO₂</td>
<td></td>
</tr>
<tr>
<td>30s</td>
<td>S9 SiO₂</td>
<td></td>
</tr>
<tr>
<td>180s</td>
<td>S10 SiO₂</td>
<td></td>
</tr>
<tr>
<td>10s</td>
<td>S11 SiO₂</td>
<td></td>
</tr>
<tr>
<td>10s</td>
<td>S12 SiO₂</td>
<td></td>
</tr>
<tr>
<td>10s</td>
<td>S13 SiO₂</td>
<td></td>
</tr>
<tr>
<td>180s</td>
<td>S14 SiO₂</td>
<td></td>
</tr>
<tr>
<td>180s</td>
<td>S15 SiO₂</td>
<td></td>
</tr>
<tr>
<td>360s</td>
<td>Wet Clean</td>
<td></td>
</tr>
<tr>
<td>10s</td>
<td>S16 SiO₂</td>
<td></td>
</tr>
<tr>
<td>10s</td>
<td>S17 SiO₂</td>
<td></td>
</tr>
</tbody>
</table>

Zr Contamination (#/cm²)
- Fast decay
- Slow decay

[NSF/SRC Engineering Research Center for Environmentally Benign Semiconductor Manufacturing]
Experiment 3 Results

- Highest Zr concentration for wafer without plasma

**A**

<table>
<thead>
<tr>
<th>Process Time</th>
<th>Wet Clean</th>
<th>SiO$_2$</th>
<th>ZrO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1800s seasoning</td>
<td>S1 SiO$_2$</td>
<td>S2 SiO$_2$</td>
<td>Z1 ZrO$_2$</td>
</tr>
<tr>
<td>60s</td>
<td>10s</td>
<td>15s</td>
<td></td>
</tr>
<tr>
<td>20s</td>
<td>15s</td>
<td>30s</td>
<td></td>
</tr>
<tr>
<td>60s</td>
<td>15s</td>
<td>120s</td>
<td></td>
</tr>
<tr>
<td>360s</td>
<td>no plasma</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**B**

<table>
<thead>
<tr>
<th>Process Time</th>
<th>Wet Clean</th>
<th>SiO$_2$</th>
<th>ZrO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1800s seasoning</td>
<td>S8 SiO$_2$</td>
<td>S9 SiO$_2$</td>
<td>Z6 ZrO$_2$</td>
</tr>
<tr>
<td>60s</td>
<td>30s</td>
<td>10s</td>
<td></td>
</tr>
<tr>
<td>30s</td>
<td>30s</td>
<td>30s</td>
<td></td>
</tr>
<tr>
<td>60s</td>
<td>30s</td>
<td>120s</td>
<td></td>
</tr>
<tr>
<td>30s</td>
<td>360s</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Increasing ZrO$_2$ Etch Time**

(SiO$_2$ Etch Time Constant)

**Increasing SiO$_2$ Etch Time**

(ZrO$_2$ Etch Time Constant)
Model Basis

- Contamination transfer rate $\propto$ vapor pressure and sticking coefficient
- Use ideal gas approximation for impingement rate
- Transfer rate coefficients are constants
- Assumptions:
  - no spatial variations
  - constant pump rate
  - no wall sputtering

ZrO$_2$ Etch

SiO$_2$ Etch
Modeling Contamination Accumulation and Decay

Where:

\[ S \cdot n_w = x \quad \text{S is chamber area} \]
\[ S_s \cdot n_s = y \quad \text{S_s is wafer area} \]
\[ V \cdot n_c = z \quad \text{V is chamber volume} \]
\[ P_{pump} / V = B \quad \text{P is pump speed} \]

\[ E = \frac{E_{zr} \cdot S_s \cdot \rho_{zr} \cdot N_A}{Weight_{zr}} \]

Boundary conditions:

At \( t = 0 \):
\[ n_w = n_o \]
\[ n_s = 0 \]
\[ n_c = 0 \]

- During \( \text{ZrO}_2 \) etch, \( k_3, k_4 = 0, b = 0 \)
- During \( \text{SiO}_2 \), \( E = 0, E_w = 0 \)
Obtaining k Constants

$k_1$ and $k_3$:
- Mass transfer from chamber to wall, chamber to SiO$_2$ wafer
- $\propto$ Zr impingement rate, $R$, times sticking coefficient
- $R \propto$ chamber partial pressure of Zr

$k_2$ and $k_4$:
- Mass transfer from wall to chamber, chamber to SiO$_2$ wafer
- Escaping rate from surface is balanced with the impingement rate at the volatility vapor pressure
- Extra sputtering term is added to $k_4$ for etching of newly deposited Zr

$k_5$:
- Mass transfer from surrounding area (re-sputtering)
Model: Experiment 1

![Graph showing Zr contamination as function of time](image)

- ZrO₂ wafer being etched
- SiO₂ wafer being etched

- Wafer concentration as function of time
- Wafer taken out at a given time

Zr Contamination (#/cm²)

- Fast decay
- Slow decay

seconds
Model: Experiment 1 (continue)

• Model fit experiment reasonably well

• Plasma concentration saturates quickly

• Wall concentration increases ~ linearly

Fitting

Wall concentration

Chamber concentration

Zoomed-in on chamber concentration
Model: Varying k’s for Experiment 1

- \( \uparrow k_1, \uparrow n_c \rightarrow \) higher wafer concentration

- \( \uparrow k_2, \uparrow \) transfer from chamber wall, \( \uparrow \) wafer concentration
- Faster decay from wall, faster total decay with time

- \( \uparrow k_3, \uparrow \) wafer impingement, \( \uparrow \) wafer concentration

- \( \uparrow k_4, \uparrow \) wafer escape, lower wafer concentration

- \( \uparrow k_5, \uparrow \) surrounding area escape, \( \downarrow \) wafer

- \( \uparrow E_w, \uparrow \) surrounding area, \( \downarrow \) wafer due to re-sputtering
Model: Experiment 2

- Same fitting parameters as experiment 1

Fitting

Wall concentration

Chamber concentration

Zoomed-in on chamber concentration
Model: Experiment 3A (SiO₂ Etch Time Constant)

- Same fitting parameters as experiment 1,2

[Graphs and charts showing fitting, wall concentration, chamber concentration, and zoomed-in view on chamber concentration]
Model: Experiment 3B (ZrO₂ Etch Time Constant)

- Same fitting parameters as experiment 3A

[Fitting](#)

[Wall concentration](#)

[Chamber concentration](#)

[Zoomed-in on chamber concentration](#)
Advantages of the Mass Transfer Model

• Straightforward kinetics model

• Model gives insight into the different time scales and sources for the transfer mechanism

• Relationship between the chamber wall and wafer surfaces in mass transfer can be seen

• Can see sensitivity of rate transfer factors (k’s)
Other Contaminants

• Initial ZrO₂ wafers have other contaminants

• Interesting behavior for Mg
  - Contaminant from walls and wafer
Conclusions and Future Application

• Cross-contamination becoming more important

• Experimental results show complex accumulation and decay behaviors

• Developed mass transfer model based on volatility and sputtering

• Reasonable fit with experimental data

• Opportunity to investigate other materials