Synergistic Effects of Gas Mixtures in a transformer-coupled toroidal plasma source for remote chamber cleaning

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Contents

- Introduction of Equipments for Remote Chamber Cleaning
- Enhancement of Fluorocarbon Etching Rate by Nitrogen
  - Nitrogen prevents recombination to form COF$_2$
- Saturation of Etching Rate
  - P$_F$ small : Linear regime $\rightarrow$ Increase NF3 Flow Rate
  - P$_F$ large : Saturation regime $\rightarrow$ Increase Temperature
- Synergistic Effect of Gas Mixtures on Nitride Film
  - Enhancement of Etching Rate
  - NF$_3$ vs. Blend
Remote Chamber Cleaning

Remote Chamber Cleaning

- Optically Interferometry: Measure etching rate, oxide film tested.

$C_{x}F_{y}$

$\text{Ar}$

$\text{O}_{2}$

Toroidal Plasma

Ferrite Core

400kHz

ASTRON made by MKS ASTEX
Power $\rightarrow$ 14kW
Power Density $\rightarrow$ 40W/cm³

PECVD Chamber

Oxide Wafer

FTIR

Line-of-sight Mass Spec

PUMP
Detailed Scheme of the Apparatus

Plasma Source
- Ferrite Core
- Gas Inlet NF3/Ar
- CxHy/Ar
- Other gases

Transfer Tube
- Capacitance Manometer
- Sapphire viewport
- 1" Ferrite Core
- 7.2"

Cleaning Chamber
- Coolant Water in
- Coolant Water out
- Mass Spec chamber
- Interferometry System
- Mass Spec
- FTIR System
- Computer
- Optical Fiber
- Monochromator
- CCD
- Computer
- FFIR
- Mass Spec system
- Turbon Pump
- Turbon Pump
- Roughing Line

Pump Set
- Blower Pump
- Boc Edwards iQMB1200F
- Dry Pump
- Boc Edwards iQDP 80
- N2 Purging Gas
- FTIR
- Exhaust Line
- Computer
Effect of addition of N2 in C4F8+O2+Ar plasmas

- Started at 250 sccm C4F8, 1750 sccm O2 and 2000 sccm Ar
- Chamber pressure 2 torr, TEOS oxide film at 100°C
- Under the same condition for 667 sccm NF3, the etching rate is 1550 Å/min.
Etching Rate Results vs FTIR

- Relaxation time 5 orders of magnitude longer than residence time
- Suggests a surface modification
FTIR Measurements v.s. Etching Rate

- Why is etching rate with CxFy smaller than NF3?
  - Loss of F to COF₂ formation

- Why does N₂ addition improve etching rate with CxFy?
  - Due to the changes in the plasmas?
  - Reduced COF₂ formation
  - Due to downstream surface?
Maybe not because of the plasma source!

- No observable change of plasma physics, with addition of $\text{N}_2$:
  - Current and voltage waveform.
  - Spatial distribution of F and O atom concentration
  - Spatial distribution of neutral temperature
  - Spatial distribution of electron temperature
- The long lived effects and slow decay strongly suggest they are due to surface modification.
Proposed surface modification mechanism

\[
CO + 2F + \ast \rightarrow COF_2 + \ast
\]

\[
CO + O + \ast \ast \rightarrow CO_2 + \ast \ast
\]
Confirmation by Mass Spectrometer

- The enhancement of etching rate by adding N$_2$ was observed for CF$_4$, C$_2$F$_6$, C$_3$F$_8$, C$_4$F$_8$.
- The enhancement of etching rate was observed for other N-containing gases like NO, NF$_3$ etc.
- Any surface modification method that can block COF$_2$ recombination site should have similar effects.
  - Transient removal of O$_2$ flow rate $\rightarrow$ Thin polymer deposition
Transient removal of O₂ flow rate

- Condition: 250 sccm C₄F₈, 1750 sccm O₂ and 2000 sccm Ar
- The method is not preferred due to polymer deposition
Saturation of N\textsubscript{2} addition

- For surface site blocking, more N\textsubscript{2} addition shouldn’t further increase the etching rate.
Summary

- For remote chamber cleaning, C₂F₆ can have comparable performance as NF₃ for the same flow rate of elemental fluorine.
- COF₂ is the key to determine the cleaning performance of fluorocarbon gases.

\[
\text{CO} + 2\text{F} + \ast \rightarrow \text{COF}_2 + \ast
\]

N atoms

\[
\text{CO} + \text{O} + ** \rightarrow \text{CO}_2 + **
\]

More F atoms
Saturation of Etching Rate in Downstream Plasma Chamber Cleaning
PECVD Chamber Cleaning

- Toroidal Plasma
- NF3 in
- Astex, 14kW
- ferrite
- Gas in
- Shower head, T=200 C
- Chamber wall, T=50 C
- Electrode, T=300 C
- Throttle valve
- Process Chamber
- Shower head
- Mounting
- SiO2+F15 → SiF4 + O2
- NF3 → 0.5 N2 + 3F
- Pump
- Exhaust
Problem: Is Maximizing NF₃ flow rate the best way to clean PECVD chamber?

- **Time to clean PECVD Chamber**
  - Three different temperature and cleaning area
    - Chamber Wall (T=50 C)
    - Shower head (T=200 C)
    - Electrode (T=300 C)

- **Conventional Cleaning Operation**
  - Maximize NF₃ Flow Rate
  - Maximize Pumping Rate to Exhaust

- **Another approach: Kinetics**
  - Adsorption limiting regime: Inlet NF₃ amount will affect etching rate
  - Reaction limiting regime: Inlet NF₃ amount will not affect etching rate
Experimental Apparatus

- Astex, 14kW
- Toroidal Plasma
- Gas in
- Shower head
- Process Chamber
- Butterfly valve
- Throttle valve
- Water Mounting
- FT-IR
- Exhaust
- Interferometry
- Line-of-sight Mass spec
- PUMP
Etching Rate vs NF3 Flow Rate

Saturation of Etching Rate

Increasing Sample Temperature

Oxide Etching Rate (Angstrom/min)

NF3 Flow Rate (sccm)

P_{chamber} = 2 \text{ Torr}
Langmuir-Hinshelwood Kinetics

- Physisorption
  - \( F(g) \rightleftharpoons F(\text{ads}) \)
- Surface Reaction
  - \( 4F(\text{ads}) + \text{SiO}_2(\text{solid}) \rightarrow \text{SiF}_4(g) + O_2(g) \)
- Two regimes:
  - Linear regime: If \( P_F \) is small, the etching rate is linearly dependent on partial pressure of fluorine. The temperature dependence is Arrhenius-like.
    \[
    ER \propto \frac{1}{\sqrt{T}} P_F \cdot e^{-\left(\frac{E_{\text{reaction}} - E_{\text{desorption}}}{RT}\right)}
    \]
  - Saturation regime: If \( P_F \) is large, the etching rate is independent of partial pressure of fluorine.
    \[
    ER \propto e^{-\frac{E_{\text{reaction}}}{RT}}
    \]
Etching rate vs F partial pressure

- Assuming complete dissociation of NF$_3$ $\rightarrow$ 0.5N$_2$ + 3F
Confirmation experiments

- To confirm above observation, we fixed the pressure of the plasma source (4 torr) and independently changed the process chamber pressure.
- Similar saturation was observed (2000Ar/2000NF3).
## Maximum Etching Rate and Threshold Fluorine Concentration

<table>
<thead>
<tr>
<th>Wafer Temperature (°C)</th>
<th>Saturation Etching Rate (Å/min)</th>
<th>Threshold partial pressure of Fluorine (torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>1230</td>
<td>~1.4</td>
</tr>
<tr>
<td>100</td>
<td>2100</td>
<td>~1.6</td>
</tr>
<tr>
<td>150</td>
<td>3600</td>
<td>~1.8</td>
</tr>
<tr>
<td>200</td>
<td>7000-8000</td>
<td>~2.2</td>
</tr>
</tbody>
</table>

- **Calculation of the threshold atomic fluorine concentration:**
  - Using the experimentally measured temperature in the source
  - Using the experimentally measured pressure in the source and in the cleaning chamber
  - Using the measured atomic fluorine concentration in the plasma source
Change of saturation threshold

\[ \text{Etching Rate} \propto [F_{\text{adsorption}}] \times \exp\left(-\frac{E_{\text{reaction}}}{RT}\right) \]

Saturation Threshold Change

\[ \ln (\text{Etching Rate}) \]

\[ \ln (\text{Reaction Rate Coefficient}) \]

\[ \ln [F_{\text{adsorption}}] \]
PECVD Chamber Cleaning

SiO2+F24 → SiF4 + O2
NF3 → 0.5 N2 + 3F
Summary

- **Saturation of Oxide Etching Rate**
  - $P_F$ small : Linear regime
  - $P_F$ large : Saturation regime
- **Saturation can be explained by Langmuir-Hinshelwood Mechanism**
- **Flamm(1979)’s Results introduced Linear Regime**
- **Optimum Condition for Chamber Cleaning**
  - Linear regime : Increase $\text{NF}_3$ flow rate
  - Saturation regime : Increase temperature
Synergistic Effect of NF$_3$ vs. Gas Blend on Nitride Film
Experimental Apparatus

Astex, 14kW

Toroidal Plasma

Gas in

ferrite

Butterfly valve

Interferometry

Line-of-sight

Mass spec

Process Chamber

Shower head

Throttle valve

Water

Temperature Controller

FT-IR

Exhaust

PUMP
Enhancement of Etching Rate

\[ \text{Nitride Etching Rate (A/min)} \]

- \( P_{\text{chamber}} = 5 \text{ torr} \), \( T_{\text{electrode}} = 50 \ ^\circ \text{C} \)
- Etching Rate increases more than 4 times that of pure \( \text{NF}_3 \)
• Only 2% of addition can make 4x change
• Tflow = 4800 sccm, $P_{\text{chamber}} = 5$ torr, $P_{\text{source}} = 5.9$ torr
Temperature Effect

![Bar Chart]

- NF3 only
- Blend-1
- Blend-2

Temperature (C): 50, 100, 150, 200

Nitride Etching Rate (A/min)
Nitride Film Etching @ Pc=2torr

Etching Condition

- Blend has advantage at higher chamber pressure
Nitride Film Etching @ Pc=3torr

Etching Condition

- NF3 only
- Mix-3
- Blend-2
- Mix-4

Nitride Etching Rate (A/min)

- Low Ps~3.3torr
- Medium Ps~3.5torr
- High Ps~4.0torr
Nitride Film Etching @ Pc=5torr

Etching Condition

Nitride Etching Rate (Å/min)

- **NF3 only**
- **Mix-3**
- **Blend-2**
- **Mix-4**

- **Low Ps~5.1torr**
- **High Ps~5.5torr**

Graph showing the etching rate for different conditions.
Oxide Film Etching @ Pc=2torr

• Blend-2 does not have advantage in etching rate on Oxide Film
Oxide Film Etching @ Pc=3torr

Ps increases

- Low Ps~3.2torr
- Medium Ps~3.5torr
- Medium-High Ps~3.7torr
- High Ps~4.0torr

• Blend-2 does not have advantage in etching rate on Oxide Film
• Blend is dominant over straight NF3
• $P_{\text{plasma source}} = 15$ torr (almost constant, choked flow)
• $T_{\text{electrode}} = 100^\circ \text{C}$, $Q_{\text{flow}} = 4800$ sccm
- Blend is dominant over straight NF$_3$
- $P_{\text{plasma source}} = 15$ torr (almost constant, choked flow)
- $T_{\text{electrode}} = 200^\circ C$, $Q_{\text{flow}} = 4800$ sccm
XPS Surface Analysis

- After running for 30 min, no significant residue on sapphire surface

![Graph showing XPS analysis results with peaks at F 1s (686), O 1s (531), Si 2p3 (102), and F (A) (832).]
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