Update on Alternative Chemistries for Dielectric Etch Applications

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Project Reports

- Unsaturated Fluorocarbon (UFC) chemistries.
- Inorganic fluorine source (NF$_3$) chemistries.
Agenda

- Chemistries examined.
- Experimental.
- Comparative process and emissions performance.
- Conclusions.
- Future work.
Chemistries Examined

- Unsaturated Fluorocarbons (UFCs):
  - octafluoro-2-butene (C\textsubscript{4}F\textsubscript{8}, CF\textsubscript{3}-CF=CF-CF\textsubscript{3}) (OF2B)
  - hexafluoropropene (C\textsubscript{3}F\textsubscript{6}, CF\textsubscript{2}=CF-CF\textsubscript{3})
  - octafluorocyclopentene (c-C\textsubscript{5}F\textsubscript{8})
  - hexafluorocyclobutene (c-C\textsubscript{4}F\textsubscript{6})
  - hexafluoro-1,3-butadiene (C\textsubscript{4}F\textsubscript{6}, CF\textsubscript{2}=CF-CF=CF\textsubscript{2}) (HF13B)
  - hexafluoro-2-butyne (C\textsubscript{4}F\textsubscript{6}, CF\textsubscript{3}-C≡C-CF\textsubscript{3}) (HF2B)

- Fluorinated Ether:
  - octafluorotetrahydrofuran (c-C\textsubscript{4}F\textsubscript{8}O)

- Perfluorocompounds (PFCs) (reference):
  - octafluoropropane (C\textsubscript{3}F\textsubscript{8})
  - octafluorocyclobutane (c-C\textsubscript{4}F\textsubscript{8})
  - n-decafluorobutane (C\textsubscript{4}F\textsubscript{10})
Experimental

• All processes run on inductively coupled high density plasma etch chamber on patterned wafers with via test structures and blanket photoresist wafers.

• Experiments carried out in three stages:
  – Investigation of all chemistries at the same process condition.
  – Further tuning of the more promising chemistries.
  – Extended time etches of the most promising chemistries.

• Via etch process performance assessed by cross sectional scanning electron microscopy (SEM).

• Emissions measured using Fourier transform infrared (FTIR) spectrometer with 10 cm cell.
  – Effluents monitored: CF₄, CHF₃, C₂F₆, C₃F₈, C₂F₄, SiF₄, HF, CO, CO₂, COF₂, and the etch gas used.
Experimental (cont.)

- Metric for reporting Global Warming Emissions:

\[ kgCE = \sum_i Q_i \times \frac{12}{44} \times GWP_{100i} \]

where \( i \) indexes each gas, \( Q_i \) is the quantity in kg of each gas, and \( GWP_{100i} \) is the global warming potential of each gas.

- Normalized Global Warming Emissions is the emissions in kgCE, scaled for a 1 µm deep etch for a nominal 0.35 µm CD via and reported in units of kgCE/µm.

- Process of comparison is a typical C\(_3\)F\(_8\) based process: Emissions = 0.316 kgCE; Via Depth = 0.8411 µm; Normalized Emissions = 0.375 kgCE/µm
Performance of Each Etch Gas at Same Process Condition

At this process condition, the C$_4$F$_6$ isomers exhibited excessive polymerization and did not etch.

It is seen that for most of the gases the major contributor to global warming emissions is the reformation of CF$_4$, CHF$_3$, and C$_2$F$_6$.

The GWPs of most UFCs are not known, but are expected to be small (~100). In addition, the destruction efficiencies for these gases are nearly complete, so their omission from the carbon equivalent calculation is unlikely to impact the global warming emissions reported.
Via Cross Sections: Typical c-C$_4$F$_8$ Process Condition

Process Conditions:
- Source Power = 1900 W
- Bias Power = 800 W
- Pressure = 6 mTorr
- Etch Gas Flow = 16 sccm
- O$_2$ Additive Flow = 0 sccm
- Etch Time = 120 s

Octafluoro-2-butene exhibited a normalized emissions reduction of 52.2%.

a: octafluoropropane
b: octafluorocyclobutane
c: n-decafluorobutane
d: octafluoro-2-butene
C₄F₆ Isomers

- Hexafluorocyclobutene
  - Normalized Global Warming Emissions Reduction: 83.2%

- Hexafluoro-1,3-butadiene
  - Normalized Global Warming Emissions Reduction: 84.2%

- Hexafluoro-2-butyne
  - Normalized Global Warming Emissions Reduction: 88.2%
Best $\text{C}_3\text{F}_6$ Process

Process Conditions:
Source Power = 1100 W
Bias Power = 1400 W
Etch Gas Flow = 12 sccm
$\text{O}_2$ Additive Flow = 0 sccm
Etch Time = 120 s

Normalized Global Warming Emissions Reduction: 76.7%
Best c-C$_5$F$_8$ Process

Process Conditions:
- Source Power = 1000 W
- Bias Power = 1150 W
- Etch Gas Flow = 11 sccm
- O$_2$ Additive Flow = 4 sccm
- Etch Time = 120 s

Normalized Global Warming Emissions Reduction: 74.0%
Best c-C₄F₈O Process

Process Conditions:
Source Power = 1000 W
Bias Power = 1000 W
Etch Gas Flow = 14 sccm
O₂ Additive Flow = 0 sccm
Etch Time = 120 s

Normalized Global Warming Emissions Reduction: 36.6%
Best Emissions Reduction for Each Gas

Reduction v. typical C3F8
Normalized Emissions Reduction
Extended Time Etch: Hexafluoro-1,3-butadiene

Process Conditions:
Source Power = 1100 W
Bias Power = 1400 W
Etch Gas Flow = 11.4 sccm
O₂ Additive Flow = 3.7 sccm
Etch Time = 4 min.

Aspect ratio: 5:1
Selectivity to resist: 6.4:1
No etch stopping.
Some CD blowout.
Conclusions

- Six UFCs and one fluorinated ether examined for dielectric etch performance. Chemistries were found to produce results similar to typical $C_3F_8$ based chemistry with lower global warming emissions.
- A hexafluoro-2-butyne process resulted in normalized emissions reduction of 88.2%. Processes based on the other $C_4F_6$ isomers resulted in normalized emissions reductions greater than 80%.
- A four minute hexafluoro-1,3-butadiene process resulted in an aspect ratio of 5:1 with good selectivity to resist and no etch stopping.
Future Work

• Further process tuning with the UFC chemistries.
• Examination of selectivity to stop layers.
• Formulate an understanding of how the molecular structure of the feed gas affects the common high-GWP effluents in the exhaust.
Acknowledgments

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• Laurie Beu
• Tra Baumeister
• Etch maintenance team at Motorola APRDL
Agenda

- Introduction and Background
- Study of NF$_3$/C$_2$H$_2$ chemistry
  - Blanket films
  - Patterned wafers
  - Supplemental Analysis
- Preliminary Study of NF$_3$/C$_2$H$_4$ chemistry
  - Patterned wafers
  - Supplemental Analysis
- Summary and Future Work
**Introduction**

These source materials lead to processes with appreciable global warming potentials for two primary reasons:

1.) The source gases themselves are global warming and are not broken up sufficiently in the plasma.

2.) The processes that use these gases tend to form CF$_4$, an extremely long-lived global warming gas.
Introduction

New Approach:

Decouple fluorine and carbon introduction to the plasma to provide more control over global warming emissions.

The idea:

Add the same atomic components to a high density plasma that are contained in a PFC-based plasma etch process to achieve the same result with few or no global warming emissions.
Introduction

The assumption:

A high density plasma environment efficiently breaks down source molecules, and it is the resulting “atomic soup” that controls the chemistry of the etch process. *Therefore, it should be possible to provide an alternative combination of carbon, fluorine, and hydrogen to achieve similar process performance.*
**NF$_3$/C$_2$H$_2$ Chemistry**

*Blanket Films*

- Varied NF$_3$ flow rate, source power, and pressure with NF$_3$/He and NF$_3$/Ar plasmas to determine blanket TEOS etch rate behavior.

  **Result:** No etching for any point tested.

- Added acetylene (C$_2$H$_2$) to the NF$_3$/He plasma and measured blanket TEOS etch rate.

  **Result:** Achieved etch rates comparable to CF$_4$/He process used as basis for comparison. (~4000 Å/min) Noticed a roughly linear increase in etch rate with increased pressure.
**NF$_3$/C$_2$H$_2$ Chemistry**

*Patterned Wafers*

- **Goal:** Screen NF$_3$/C$_2$H$_2$ chemistry in a dielectric etch application (high aspect ratio TEOS via etch); characterize process performance over wide range of tool parameters.

- **Process tool:** Inductively coupled high density plasma etch tool

- **Effects examined:**
  - NF$_3$ and C$_2$H$_2$ flow rates (and implied fluorine:carbon ratio)
  - Source and Bias Power
  - Pressure
  - Temperature

- **Significant results:**
  - Successfully etched features of 0.6, 0.45, and 0.35 µm nominal printed CD with etch rates up to 6300 Å/min.
  - Achieved photoresist selectivity up to 12.5, and lag as low as 5.6% from 0.6 µm to 0.35 µm.
  - No observed negative process impact on tool.
**NF$_3$/C$_2$H$_2$ Chemistry**

*Patterned Wafers*

Comparison of 0.35 µm (nominal printed CD) vias etched with a C$_3$F$_8$ process for 2 minutes (left), an NF$_3$/C$_2$H$_2$ process for 2 minutes (center), and a slightly different NF$_3$/C$_2$H$_2$ process for 3 minutes (right).
NF$_3$/C$_2$H$_2$ Chemistry

Optical Emissions

OES Results -- CF$_4$ and NF$_3$/C$_2$H$_2$

- NF$_3$/C$_2$H$_2$ process
- CF$_4$ process

Wavelength (nm)

Intensity/1000

NF$_3$/C$_2$H$_2$ processes show emissions at various wavelengths, including CN, SiF, C$_2$, H, He, F, and SiF, compared to CF$_4$ processes.
**NF$_3$/C$_2$H$_2$ Chemistry**

**Emissions Results**

- All emissions calculations use revised GWP values, and account for all global warming species detected, including CO$_2$ and CH$_4$.

<table>
<thead>
<tr>
<th>Process (2 min. etch)</th>
<th>Global Warming Emissions (kgCE)</th>
<th>% Reduction from C$_3$F$_8$ process</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_3$F$_8$/CH$_3$F</td>
<td>0.3156</td>
<td></td>
</tr>
<tr>
<td>NF$_3$/C$_2$H$_2$—Lowest emissions</td>
<td>0.059</td>
<td>81%</td>
</tr>
<tr>
<td>NF$_3$/C$_2$H$_2$—Highest emissions</td>
<td>0.147</td>
<td>53%</td>
</tr>
<tr>
<td>NF$_3$/C$_2$H$_2$—Best Process</td>
<td>0.079</td>
<td>75%</td>
</tr>
</tbody>
</table>
**NF$_3$/C$_2$H$_2$ Chemistry**

**Emissions Results**

*Detailed emissions breakdown for several process points:*

<table>
<thead>
<tr>
<th>Process</th>
<th>kgCE</th>
<th>% NF$_3$</th>
<th>% CHF$_3$</th>
<th>% CF$_4$</th>
<th>NF$_3$ UE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Best emissions</td>
<td>0.059</td>
<td>86%</td>
<td>11%</td>
<td>3%</td>
<td>95.42%</td>
</tr>
<tr>
<td>Best process</td>
<td>0.079</td>
<td>85%</td>
<td>9%</td>
<td>3%</td>
<td>91.27%</td>
</tr>
</tbody>
</table>
**NF$_3$/C$_2$H$_2$ Chemistry**

**TOF-SIMS Results**

- Approximately 200-500 Å of polymer film was deposited on TEOS with NF$_3$/C$_2$H$_2$ chemistry.
- Depth profile showed prominent intensity of H, C, F, and some level of O in the polymer film.
- Mass spectra acquired from top surface showed C$^+$, hydrocarbon ions, F$^-$, and CN$^-$.  
- Although F$^-$ peak was prominent, *common fluorocarbon peaks were absent or detected at very low intensity, suggesting polymer was primarily hydrocarbons instead of fluorocarbons.*
- Presence of CN$^-$ ions suggests inclusion of CN bonds in polymer.
NF$_3$/C$_2$H$_4$ Chemistry  
*Patterned Wafers*

- **Goal:** Complete preliminary screening of NF$_3$/C$_2$H$_4$ chemistry for oxide etch application; compare results to those attained with NF$_3$/C$_2$H$_2$
- **Process tool:** inductively coupled high density plasma etch tool
- **Effects examined:**
  - C$_2$H$_4$ flow rates (fluorine:carbon ratio)
  - Source and Bias Power
  - Pressure
- **Observations:**
  - Etch rates were markedly lower than NF$_3$/C$_2$H$_2$ processes -- increased polymerization, more H to scavenge free F.
  - Achieved very high photoresist selectivity in some cases (up to 57 -- in combination with very low etch rate), but in general selectivity equivalent to or worse than NF$_3$/C$_2$H$_2$ processes.
  - No observed negative process impact on tool, although plasma at very low F:C ratios was difficult to sustain.
NF$_3$/C$_2$H$_4$ Chemistry
Patterned Wafers

A process comparison: 0.35 µm (nominal printed CD) via etched with similar NF$_3$/C$_2$H$_2$ (left) and NF$_3$/C$_2$H$_4$ (right) processes. Decreased resist selectivity and etch rate with the NF$_3$/C$_2$H$_4$ process under these conditions.
NF$_3$/C$_2$H$_4$ Chemistry

Emissions Results

- All emissions calculations used revised GWP values, and account for all global warming species detected, including CO$_2$ and CH$_4$.

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</tr>
<tr>
<td>NF$_3$/C$_2$H$_4$—</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lowest emissions</td>
<td>0.101</td>
<td>68%</td>
</tr>
<tr>
<td>NF$_3$/C$_2$H$_4$—</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Highest emissions</td>
<td>0.149</td>
<td>53%</td>
</tr>
</tbody>
</table>

- Emissions breakdown from 0.101 kgCE point:
  - 95% NF$_3$, 3% CHF$_3$, 1% CF$_4$ [NF$_3$ utilization efficiency = 87.1%]
Summary

• NF₃ + hydrocarbon chemistry shows promise as a possible alternative to fluorocarbons.

• Substantially reduced global warming emissions (approximately 80% relative to typical C₃F₈ process) have been demonstrated with the NF₃/C₂H₂ chemistry.

• Future Work:
  – Further optimize process for selectivity and etch rate
  – More fully characterize emissions and plasma
  – Further examine chamber effects (reliability, parts erosion, etc.)
  – Test NF₃ with other hydrocarbons
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