Update on Alternative Chemistries for Dielectric Etch Applications

Ritwik Chatterjee, Laura Pruette, Simon Karecki, Rafael Reif

MIT Microsystems Technology Laboratories

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_4F_8, CF_3-CF=CF-CF_3) (OF2B)
  - hexafluoropropene (C_3F_6, CF_2=CF-CF_3)
  - octafluorocyclopentene (c-C_5F_8)
  - hexafluorocyclobutene (c-C_4F_6)
  - hexafluoro-1,3-butadiene (C_4F_6, CF_2=CF-CF=CF_2) (HF13B)
  - hexafluoro-2-butyne (C_4F_6, CF_3-C≡C-CF_3) (HF2B)
- Fluorinated Ether:
  - octafluorotetrahydrofuran (c-C_4F_8O)
- Perfluorocompounds (PFCs) (reference):
  - octafluoropropane (C_3F_8)
  - octafluorocyclobutane (c-C_4F_8)
  - n-decafluorobutane (C_4F_{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: CF_4, CHF_3, C_2F_6, C_3F_8, C_2F_4, SiF_4, HF, CO, CO_2, COF_2, and the etch gas used.

Experimental (cont.)

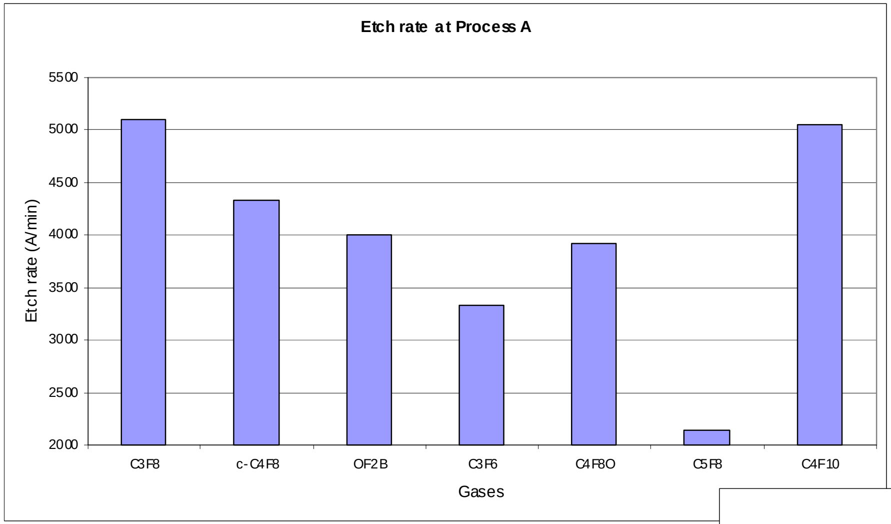
- Metric for reporting Global Warming Emissions:

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

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.

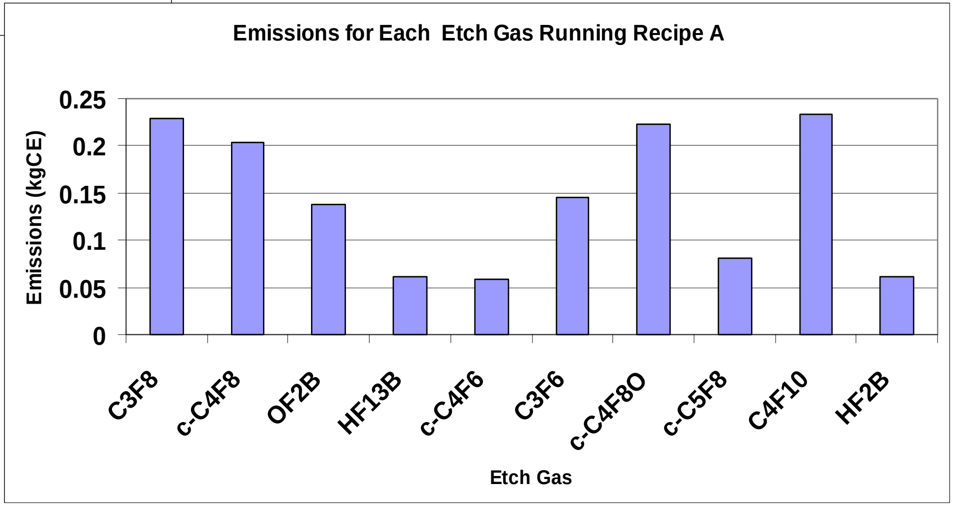
- Normalized Global Warming Emissions is the emissions in kgCE, scaled for a 1 μm deep etch for a nominal 0.35 μm CD via and reported in units of kgCE/μm.
- Process of comparison is a typical C_3F_8 based process: Emissions = 0.316 kgCE ; Via Depth = 0.8411 μm; Normalized Emissions = 0.375 kgCE/μm

Performance of Each Etch Gas at Same Process Condition



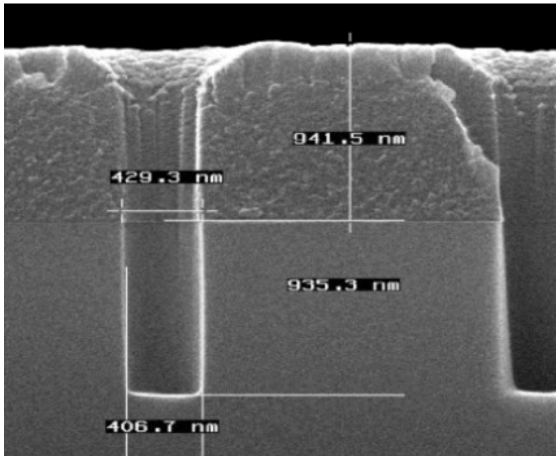
At this process condition, the C_4F_6 isomers exhibited excessive polymerization and did not etch.

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_2F_6.

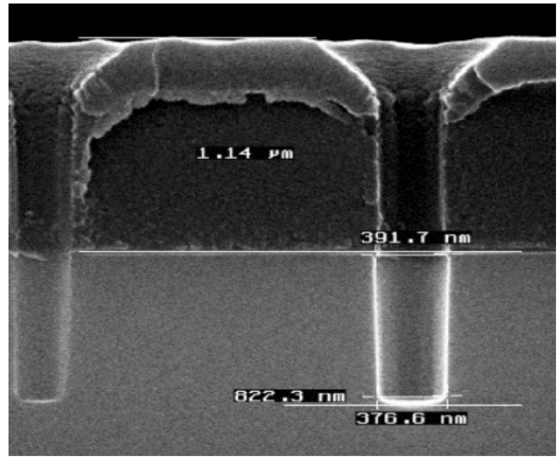


The GWPs of most UFCs are not known, but are expected to be small (~100). In addition, the destruction efficiencies for these gases are nearly complete, so their omission from the carbon equivalent calculation is unlikely to impact the global warming emissions reported.

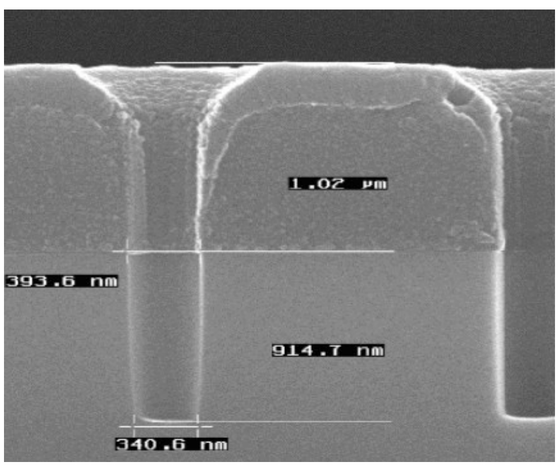
Via Cross Sections: Typical c-C_4F_8 Process Condition



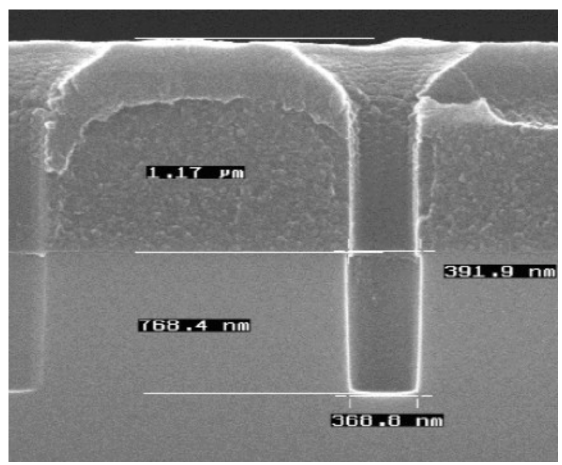
a: octafluoropropane



b: octafluorocyclobutane



c: n-decafluorobutane

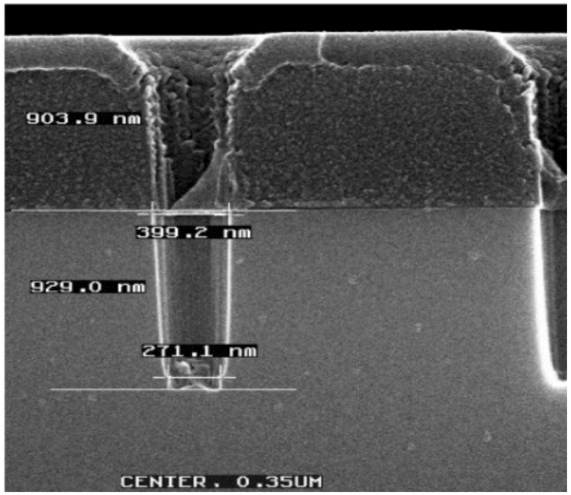


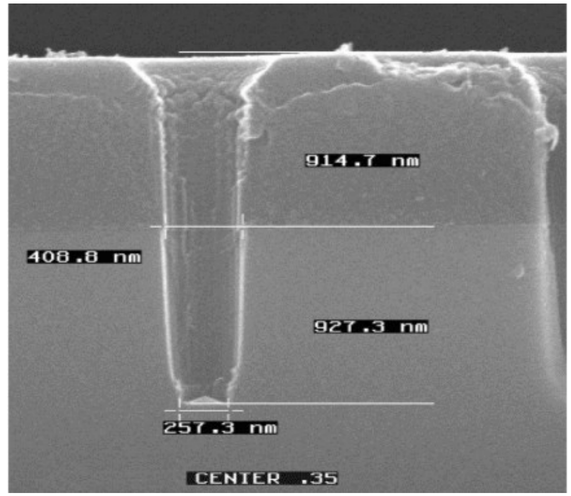
d: octafluoro-2-butene

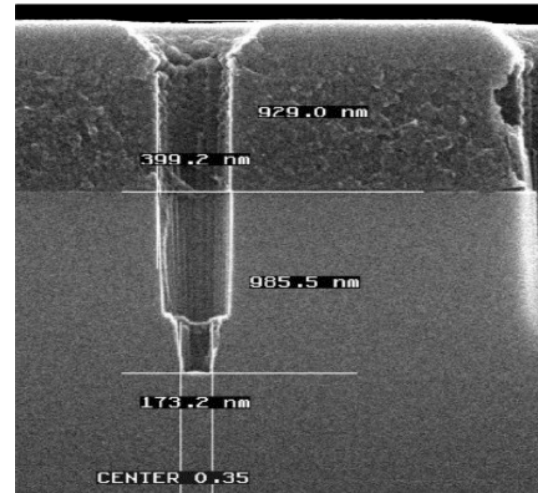
Process Conditions:
Source Power = 1900 W
Bias Power = 800 W
Pressure = 6 mTorr
Etch Gas Flow = 16 sccm
O_2 Additive Flow = 0 sccm
Etch Time = 120 s

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

C_4F_6 Isomers







hexafluorocyclobutene

Normalized Global Warming Emissions Reduction: 83.2%

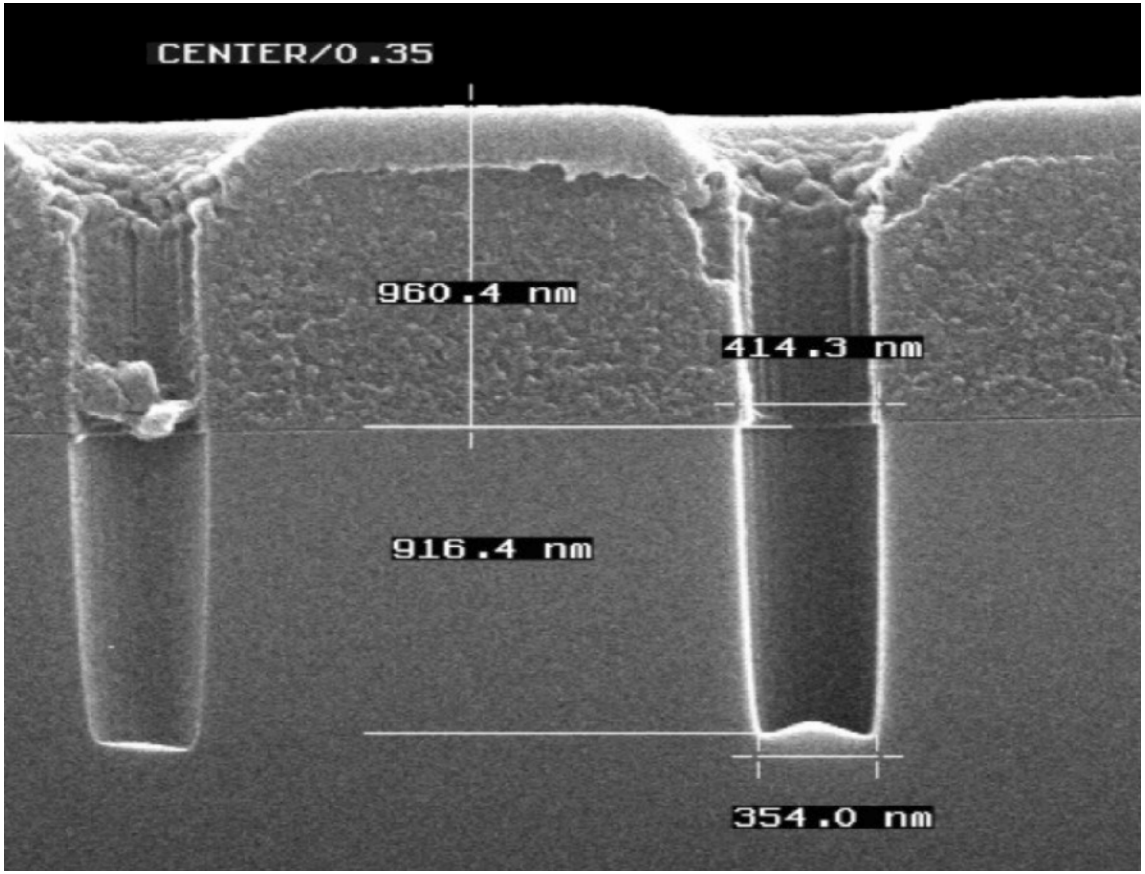
hexafluoro-1,3-butadiene

Normalized Global Warming Emissions Reduction: 84.2%

hexafluoro-2-butyne

Normalized Global Warming Emissions Reduction: 88.2%

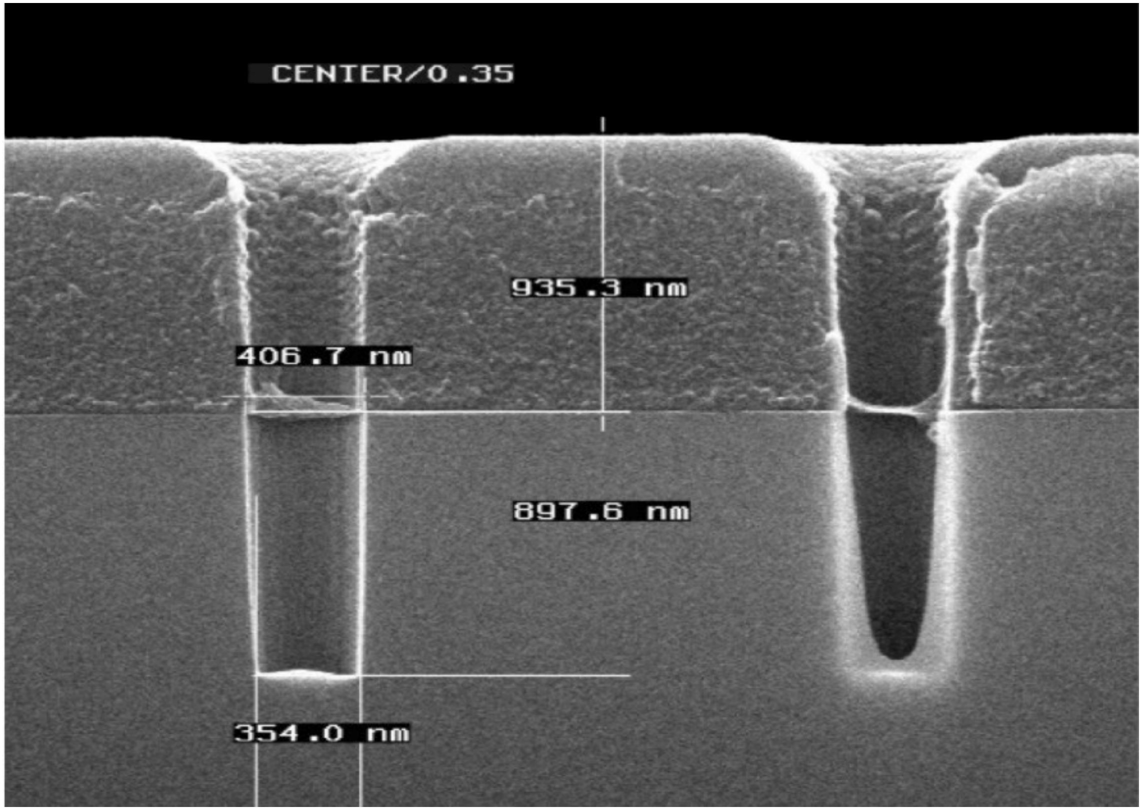
Best C_3F_6 Process



Process Conditions:
Source Power = 1100 W
Bias Power = 1400 W
Etch Gas Flow = 12 sccm
O_2 Additive Flow = 0 sccm
Etch Time = 120 s

Normalized Global Warming Emissions Reduction: 76.7%

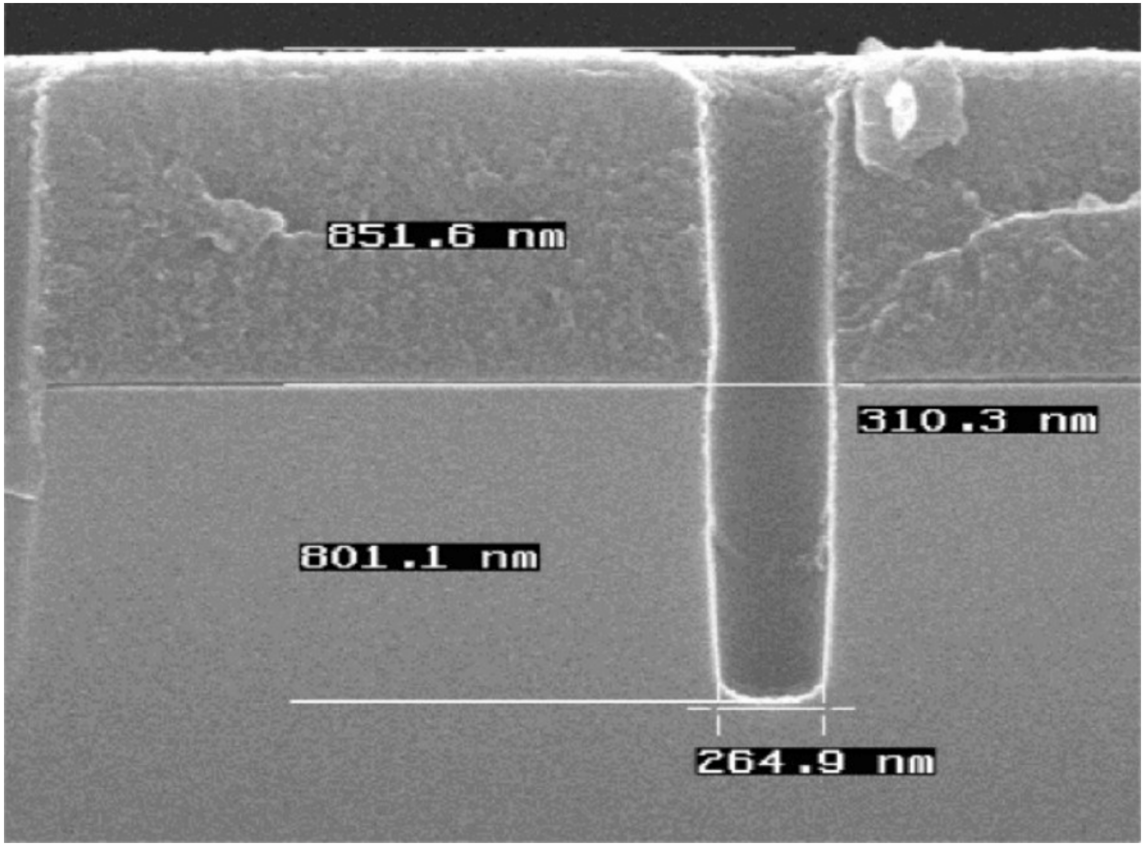
Best c-C_5F_8 Process



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%

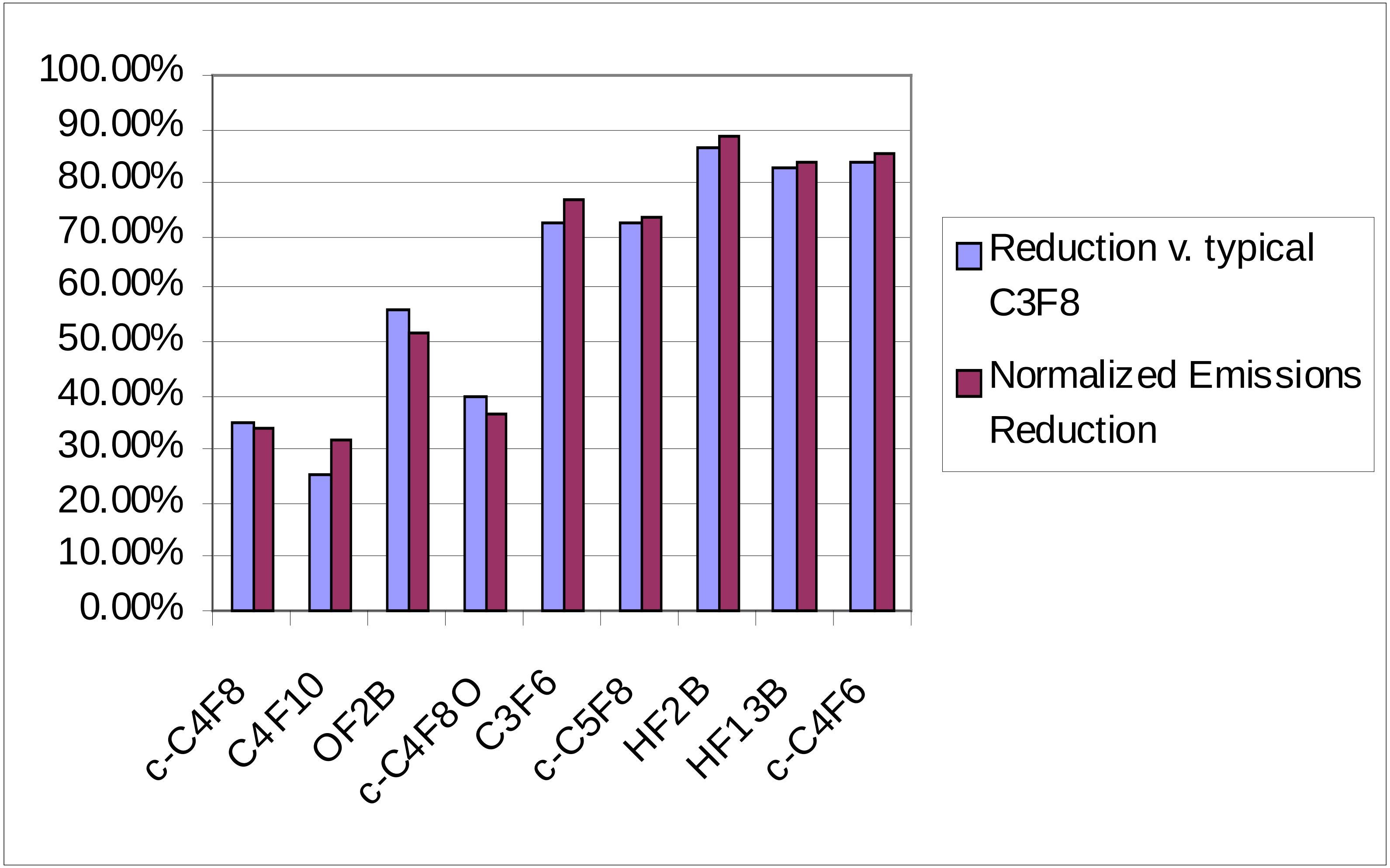
Best c-C_4F_8O Process



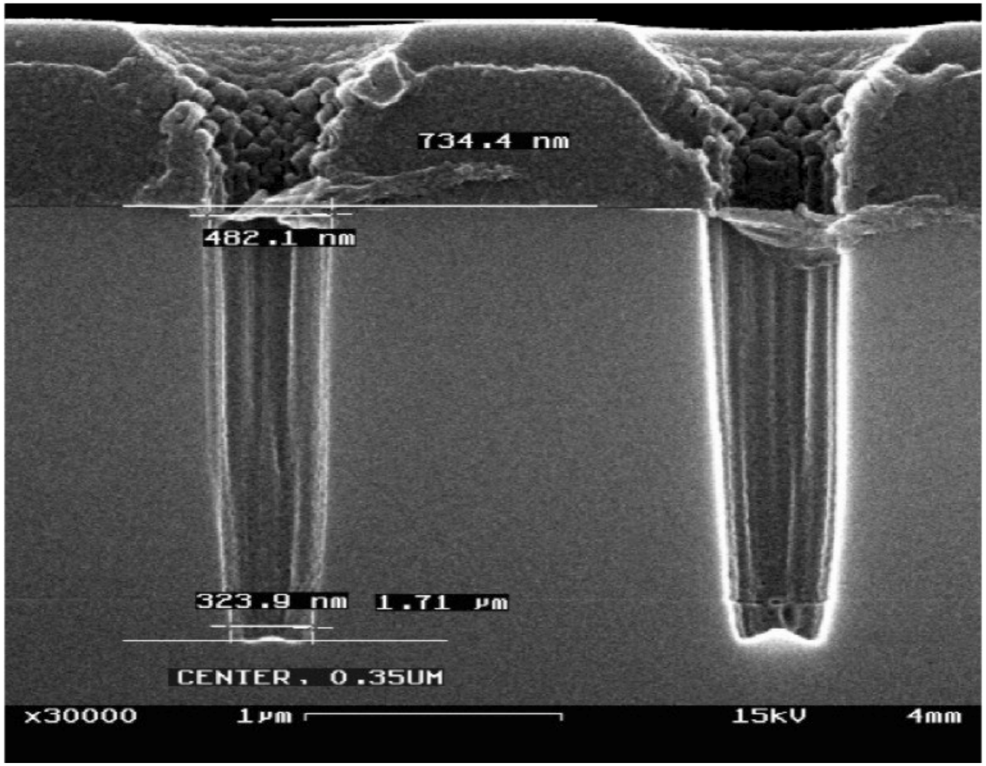
Process Conditions:
Source Power = 1000 W
Bias Power = 1000 W
Etch Gas Flow = 14 sccm
O_2 Additive Flow = 0 sccm
Etch Time = 120 s

Normalized Global Warming Emissions Reduction: 36.6%

Best Emissions Reduction for Each Gas



Extended Time Etch: Hexafluoro-1,3-butadiene



Process Conditions:
Source Power = 1100 W
Bias Power = 1400 W
Etch Gas Flow = 11.4 sccm
O_2 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

- NSF/SRC Engineering Research Center for Environmentally Benign Semiconductor Manufacturing
- Laurie Beu
- Tra Baumeister
- Etch maintenance team at Motorola APRDL

Agenda

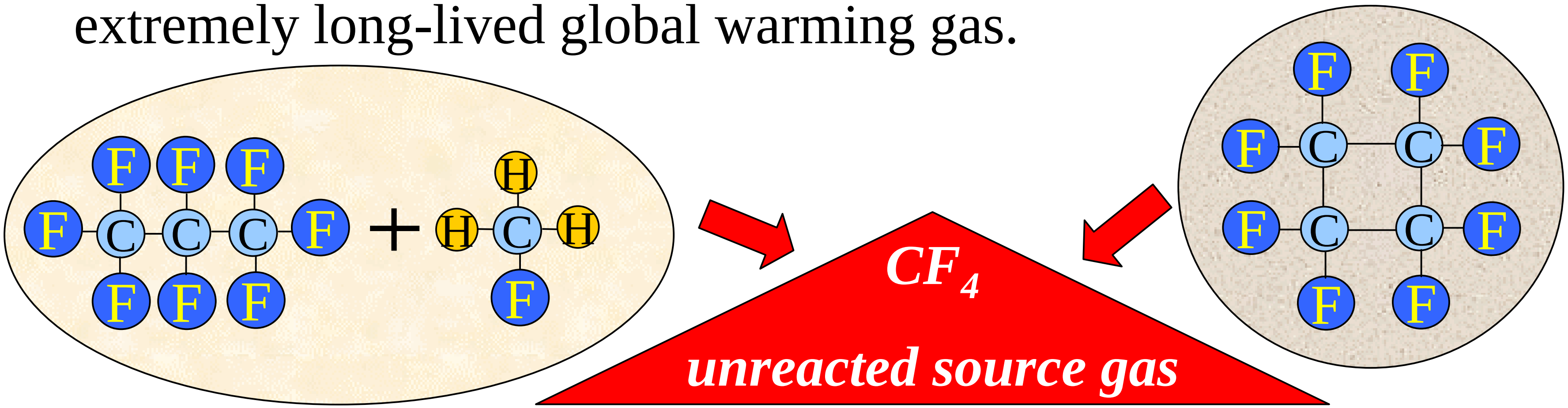
- Introduction and Background
- Study of NF_3/C_2H_2 chemistry
  - Blanket films
  - Patterned wafers
  - Supplemental Analysis
- Preliminary Study of NF_3/C_2H_4 chemistry
  - Patterned wafers
  - Supplemental Analysis
- Summary and Future Work

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:

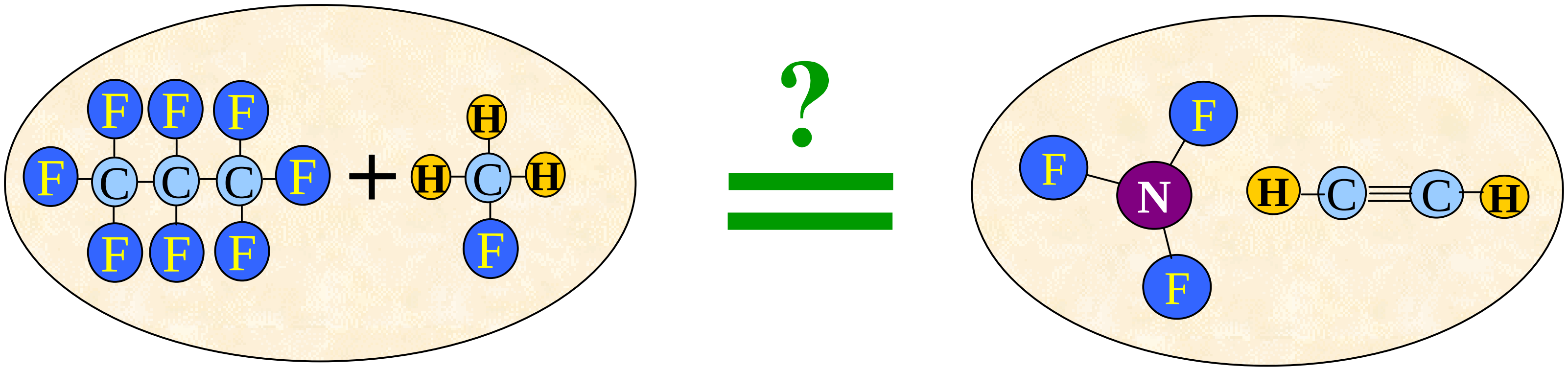
Add the **same atomic components** to a high density plasma that are contained in a PFC-based plasma etch process to **achieve the same result with few or no global warming emissions**.

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.



Conventional Process ***Novel Process***

NF_3/C_2H_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_2H_2) to the NF_3/He plasma and measured blanket TEOS etch rate.

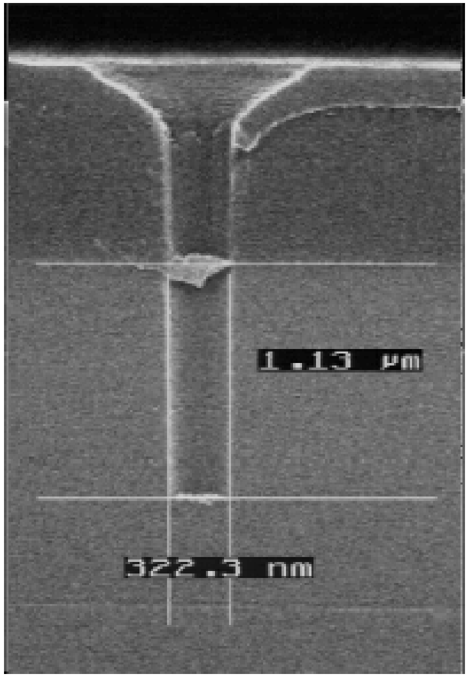
  Result: Achieved etch rates comparable to CF_4/He process used as basis for comparison. (~4000 Å/min) Noticed a roughly linear increase in etch rate with increased pressure.

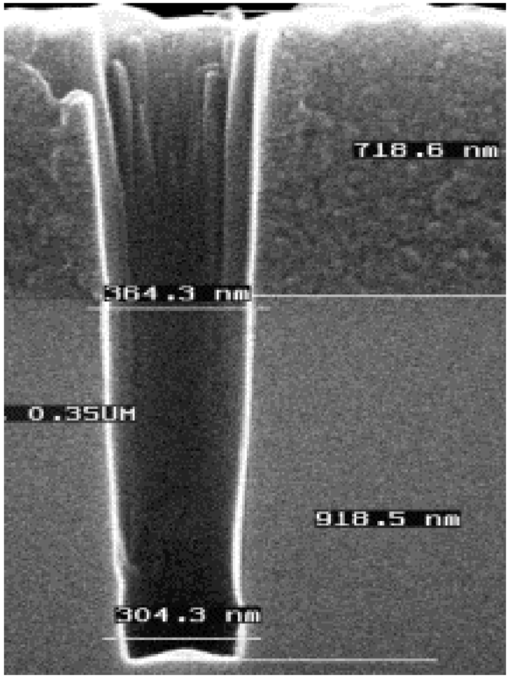
NF_3/C_2H_2 Chemistry
Patterned Wafers

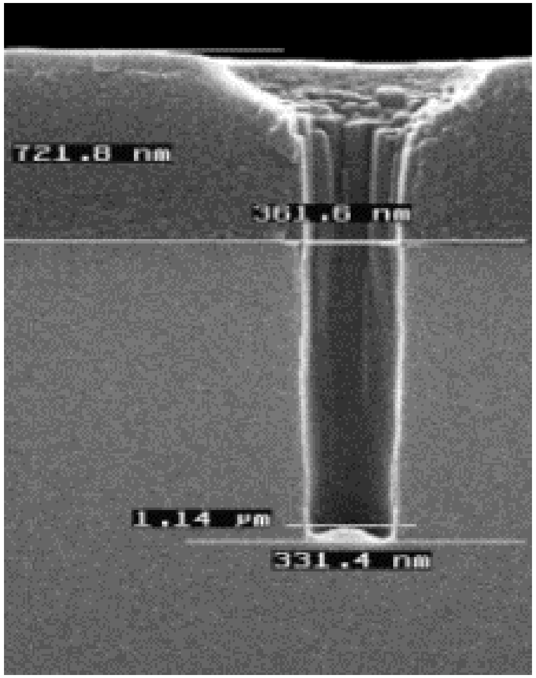
- **Goal:** Screen NF_3/C_2H_2 chemistry in a dielectric etch application (high aspect ratio TEOS via etch); characterize process performance over wide range of tool parameters.
- **Process tool:** inductively coupled high density plasma etch tool
- **Effects examined:**
  - NF_3 and C_2H_2 flow rates (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_2H_2 Chemistry

Patterned Wafers



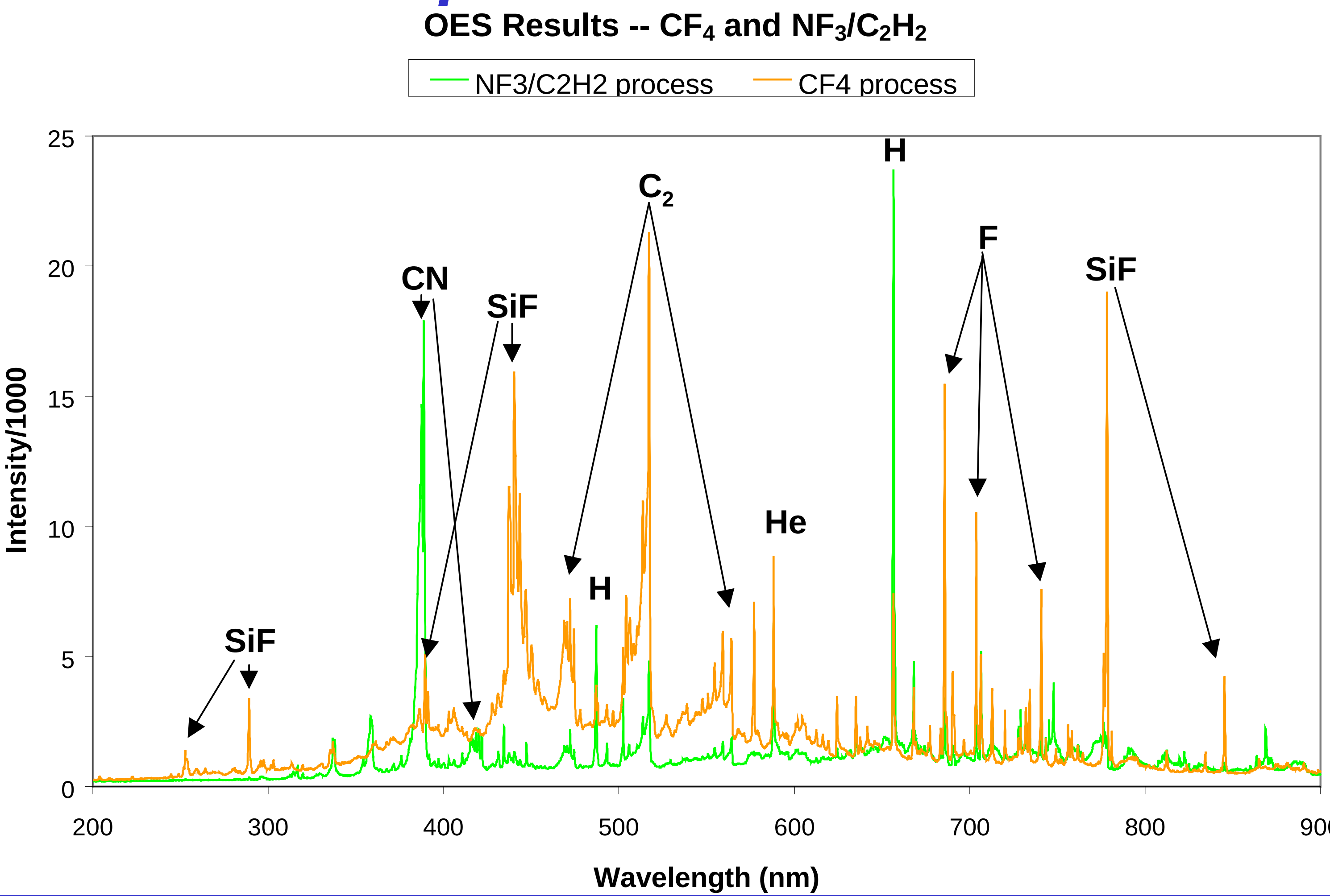




Comparison of 0.35 μm (nominal printed CD) vias etched with a C_3F_8 process for 2 minutes (left), an NF_3/C_2H_2 process for 2 minutes (center), and a slightly different NF_3/C_2H_2 process for 3 minutes (right).

NF_3/C_2H_2 Chemistry

Optical Emissions



NF_3/C_2H_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.

Process (2 min. etch)	Global Warming Emissions (kgCE)	% Reduction from C_3F_8 process
C_3F_8/CH_3F	0.3156	
NF_3/C_2H_2— Lowest emissions	0.059	81%
NF_3/C_2H_2— Highest emissions	0.147	53%
NF_3/C_2H_2— Best Process	0.079	75%

NF_3/C_2H_2 Chemistry
Emissions Results

Detailed emissions breakdown for several process points:

Process	kgCE	% NF_3	% CHF_3	% CF_4	NF_3 UE (%)
Best emissions	0.059	86%	11%	3%	95.42%
Best process	0.079	85%	9%	3%	91.27%

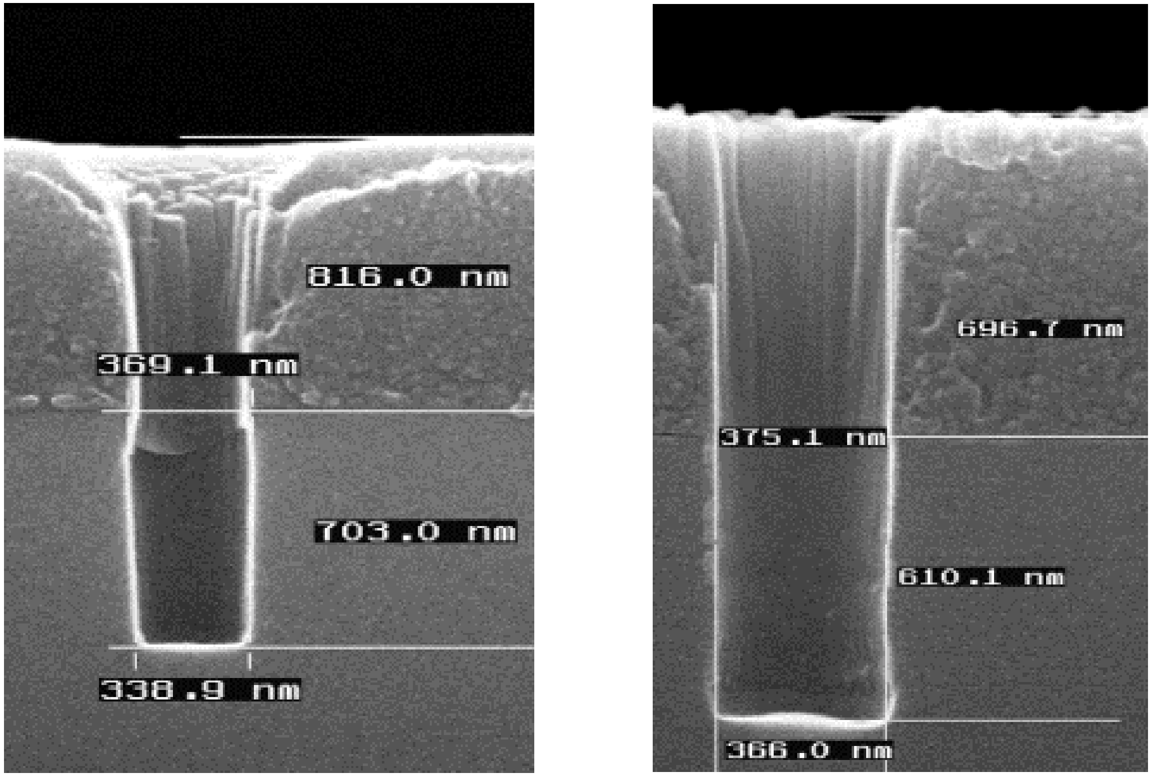
NF_3/C_2H_2 Chemistry
TOF-SIMS Results

- Approximately 200-500 Å of polymer film was deposited on TEOS with NF_3/C_2H_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_2H_4 Chemistry
Patterned Wafers

- **Goal:** Complete preliminary screening of NF_3/C_2H_4 chemistry for oxide etch application; compare results to those attained with NF_3/C_2H_2
- **Process tool:** inductively coupled high density plasma etch tool
- **Effects examined:**
  - C_2H_4 flow rates (fluorine:carbon ratio)
  - Source and Bias Power
  - Pressure
- **Observations:**
  - Etch rates were markedly lower than NF_3/C_2H_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_2H_2 processes.
  - No observed negative process impact on tool, although plasma at very low F:C ratios was difficult to sustain.

NF_3/C_2H_4 Chemistry
Patterned Wafers



A process comparison: 0.35 μm (nominal printed CD) via etched with similar NF_3/C_2H_2 (left) and NF_3/C_2H_4 (right) processes. Decreased resist selectivity and etch rate with the NF_3/C_2H_4 process under these conditions.

NF_3/C_2H_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.

Process (2 min. etch)	Global Warming Emissions (kgCE)	% Reduction from C_3F_8 process
C_3F_8/CH_3F	0.3156	
NF_3/C_2H_4— Lowest emissions	0.101	68%
NF_3/C_2H_4— Highest emissions	0.149	53%

- Emissions breakdown from 0.101 kgCE point:
  - 95% NF_3, 3% CHF_3, 1% CF_4 [NF_3 utilization efficiency = 87.1%]

Summary

- NF_3 + hydrocarbon chemistry shows promise as a possible alternative to fluorocarbons.
- Substantially reduced global warming emissions (approximately 80% relative to typical C_3F_8 process) have been demonstrated with the NF_3/C_2H_2 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 NF_3 with other hydrocarbons

Acknowledgments

- Motorola APRDL personnel who supported the project:
  - Dan Babbitt
  - Tra Baumeister
  - Laurie Beu
  - Ralph Garza
  - Lloyd Gonzales
  - Laura Mendicino
  - Jeff Rose
- International SEMATECH, which has provided additional funding for the project.