The Transition from Saturated (c-C_4F_8) to Unsaturated (1,3-C_4F_6) Perfluorocarbons: Effects on Selectivity and ARDE in Via-hole Plasma Etch Applications

Teressa L. Anglinmatumona
***Presently with Intel Corporation**
Co-author: Calvin T. Gabriel (AMD)

NCCAVS PEUG, Sunnyvale, CA
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(Submicron Development Center)

Etch Module

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Outline

- Research Motivation
- Experimental Set-up
- 1,3-C_4F_6 Characterization
- 1,3-C_4F_6 vs. c-C_4F_8

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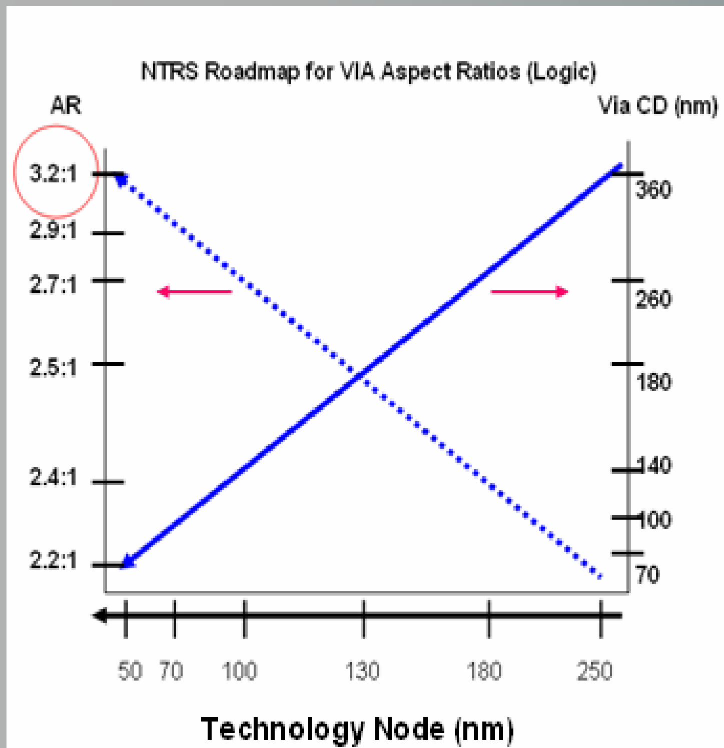
Motivation: Plasma Chemistry for HAR Dielectric Etching Beyond 65 nm Node



At a technology node of 50 nm: AR=3.2:1 and Via CD = 70 nm

Challenges:

- Mass transport limitation due to higher molecular-weight radicals.
- Thin 193 nm Resist (low etch resistance)
- Low Etch Selectivity
- ARDE

In this research, the transition from a saturated (c-C_4F_8, C-C bond) to an unsaturated (1,3-C_4F_6, C=C bond) plasma gas was found to lessen the challenges of low selectivity, anisotropy and ARDE..

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Ref. L. Ling, J. Vac. Sci. Technol. **B22** (2004) 2594.
S. Samukawa and T. Mukai: J. Vac. Sci. Technol. **B18** (2000) 166.

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Evolution of Dielectric Etch Chemistries

Saturated

Transition

Unsaturated

PFC Molecules	F/C Composition Ratio	Ionization Potential eV	Lowest Triplet (T_1) eV	Type of PFC Molecules
CF_4	4	16.2	14.73	Open-Chain Saturated PFC
C_2F_6	3	14.6	12.86	
C_3F_8	2.7	13.4	11.62	
c-C_3F_6	2	11.3	8.20	Cyclic Saturated PFC
c-C_4F_8	**2**	**11.8**	**8.49**	
C_2F_4	2	10.28	4.57	Open-Chain Unsaturated PFC with One C=C Bond
C_3F_6	2	10.62	4.30	
1-C_4F_8	2	--------	4.11	
2-C_4F_8	2	11.2	3.84	
c-C_4F_6	1.5	--------	4.60	Cyclic Unsaturated PFC with One C=C Bond
c-C_5F_8	1.6	--------	4.30	
1,3-C_4F_6	**1.5**	**9.5**	**3.94**	Open-Chain Unsaturated PFC With Two C=C Bonds
1,3-C_5F_8	1.6	--------	3.56	

1,3-C_4F_6 Process-Multiple Advantages are Driven By:

❖Unique cleaving mechanism which allows a better bond decomposition scheme (CF2 & CF3)

❖Lower energy thresholds (i.e., ionization, dissociation and excitation).

❖Lower fluorine-to-carbon (F/C) ratio.

❖More polymer-initiating radicals

[1] T. Nakamura, H. Motomura and K. Tachibana: Jpn. J. Appl. Phys. **40** (2001) 847.
[2] S. Samukawa, T. Mukai, and K. Tsuda: J. Vac. Sci. Technol. A**17** (1999) 2551.
[3] G.K. Jarvis, K.J. Boyle, C.A. Mayhew and R.P. Tuckett: J. Phys. Chem. A **102** (1998) 3230.
[4]U.S. Secretary of Commerce on Behalf of the USA, "NIST Chemistry Webbook" http://webbook.nist.gov/chemistry/.

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Experimental Set-up

Phase I

❖1,3-C_4F_6 Characterization

❖Identify Process Window in design space w/ Trade-offs

Phase II

1,3-C_4F_6 vs. c-C_4F_8 (Etch Performance)

Phase III

Develop ARDE Models (1,3-C_4F_6 vs. c-C_4F_8)

❖ Critical Aspect Ratio

Plasma Etch System:

AMAT® IPS Etcher

2^3 Factorial Design → Axial or Face Points (CCD) or (CCF) → Response Surface CCD or CCF (K=3)

Chamber Pressure (mTorr)

RF Bias Power (W)

Cathode Temp (deg C)

1st Order Model

2nd Order Model

- Factorial Points
- Axial Points
- Center Points
- Face Points

(Y) Chamber Pressure (mTorr)

(Z) RF bias Power (W)

(X) Cathode Temp (deg C)

Montgomery (1997)

ARDE Model-Based Method (i.e., RIE Lag)
(Joubert, 1994)

Modulated Etch Time= E_T= [Oxide Target Thickness (Å)]/[Oxide ER (Å/min)]

>>>>>>>>>>>>Polymer build up grossly impedes oxide etching over time

Via Depth

Polymer

$E_T=t_o$ $E_T=t_o+\Delta t$ $E_T=t_o+2\Delta t$ $E_T=t_o+3\Delta t$ $E_T=t_o+t\infty$

Fluorocarbon polymer builds up with increasing etch time.
∴ Plasma chemistry performance at the wafer substrate becomes critical.

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Trade-Offs

Order of Priority

1. **Anisotropy**

(most critical parameter to control)

2. **Oxide:Resist SEL**
3. **Oxide:Nitride SEL**
4. **Oxide Etch Rate**

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Process Trends Using 1,3-C_4F_6

Controlling Factors	PR ER	Ox ER	Nitride ER	Ox:PR SEL	Ox:Nit SEL	Profile Slope
↑ Cathode Temp	–	+	+/–	–	–	+
↑ RF Bias Power	–	+	+/–	–	+	+
↓ Pressure	+	+	+/–	+	+	+

Favorable (+) and Unfavorable (–)

*****With interaction influence**

Cathode Temp 1/∝ Polymer deposition rate

Pressure 1/∝ Ion Energy Flux

RF Bias Power ∝ Ion Energy Flux

Lower pressure ⟶ Longer mean free path- Improved directionality

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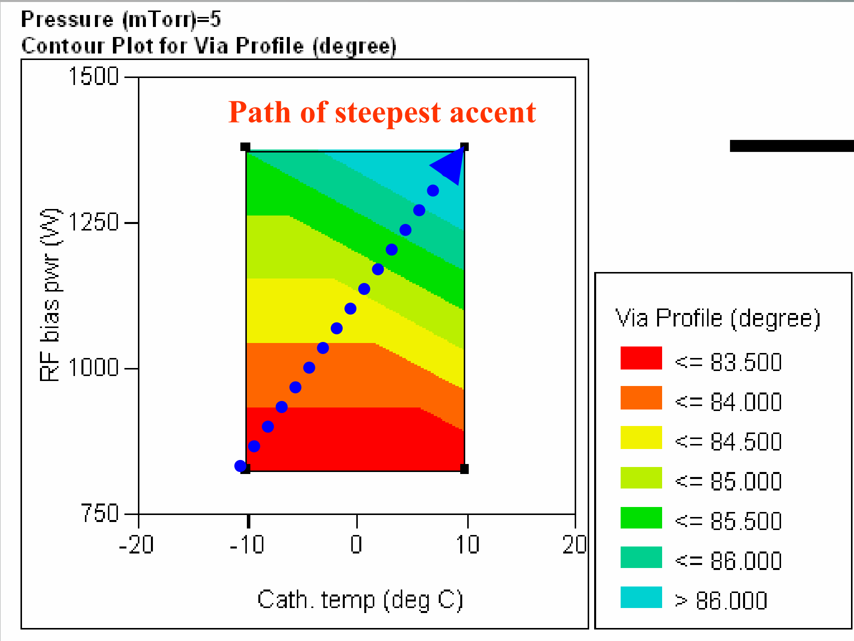
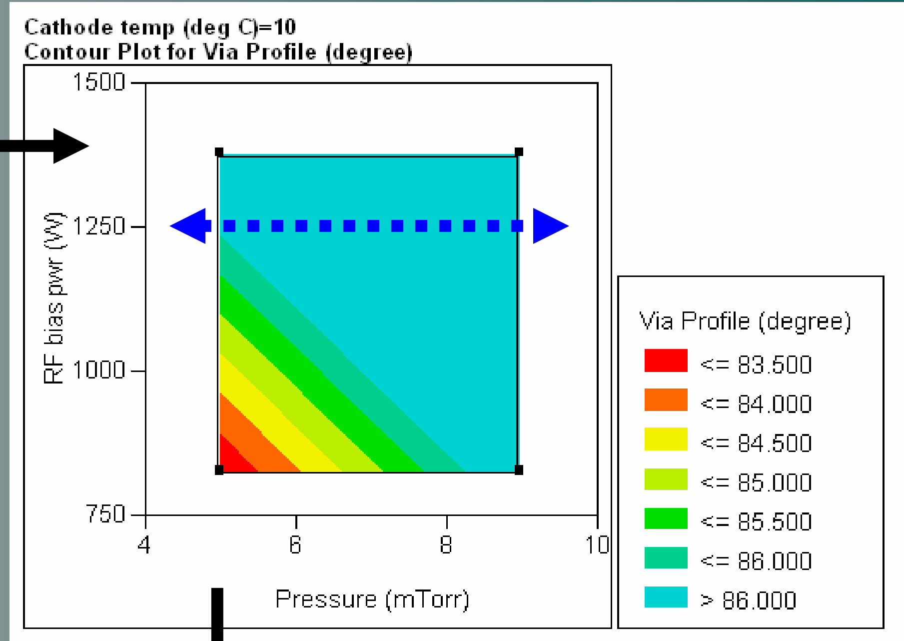
Profile Slope (i.e., Anisotropy) Using 1,3-C_4F_6

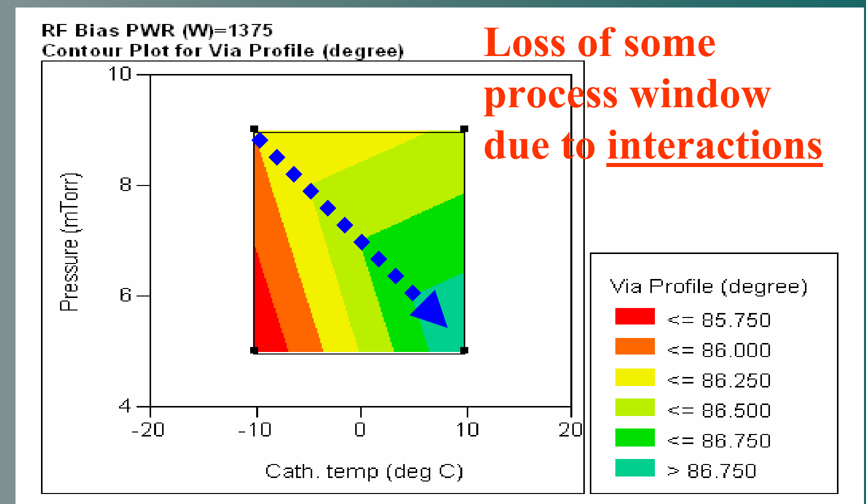




At 5 mTorr, profile slope increases with RF bias power at low/high cathode temp.

Above 1250 W and 10 deg C, profile slope is independent of pressure.

At a RF bias power of 1375 W, profile slope increases with lower pressure and higher cathode temp.



Loss of some process window due to interactions

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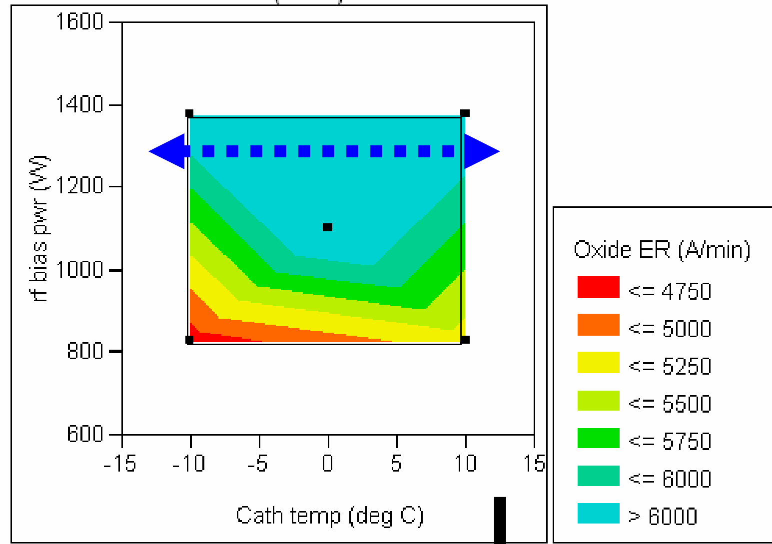
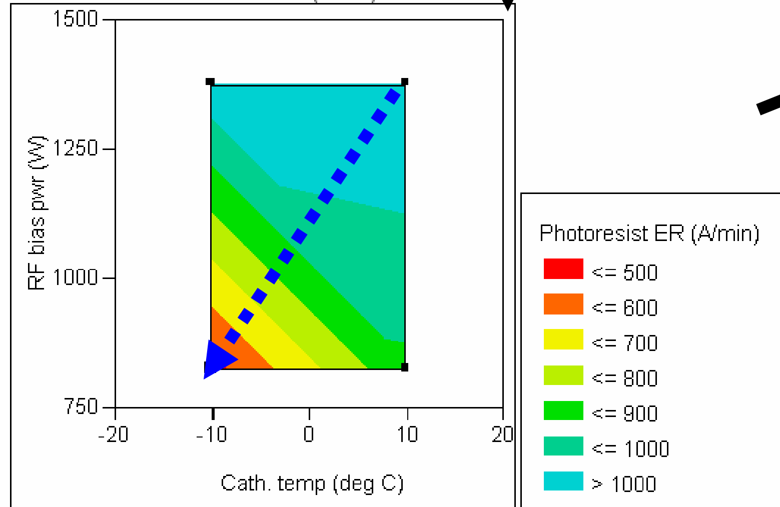
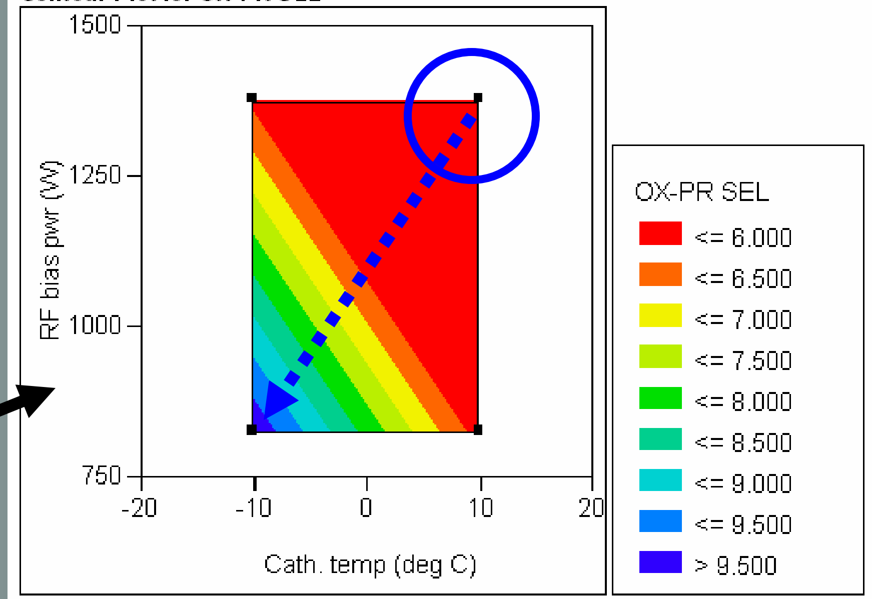
Oxide:Resist Selectivity Using 1,3-C_4F_6







❖Lower cathode temp/Lower rf bias power compromise anisotropy.

❖ An acceptable selectivity at most 6:1 can be obtained at high rf bias power and cathode temp.

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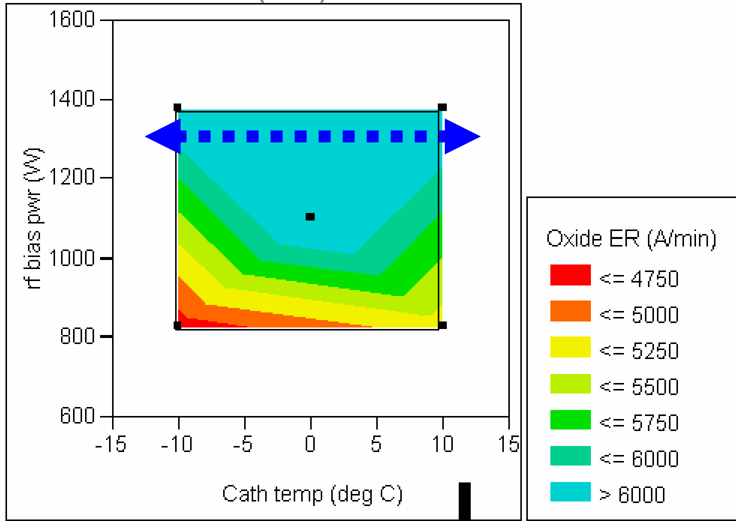
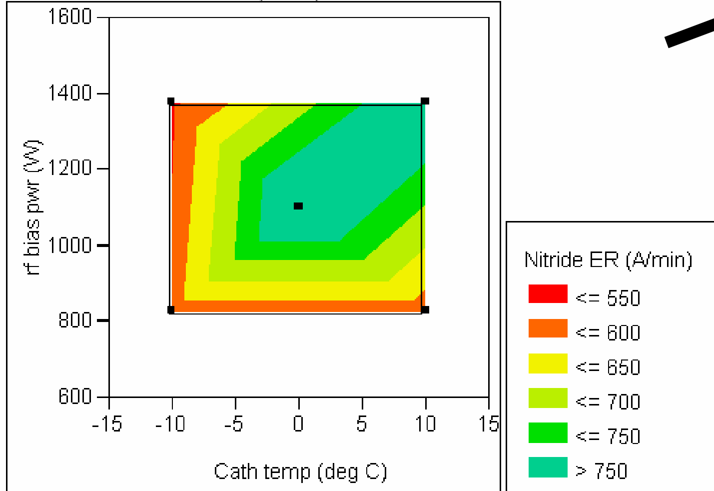
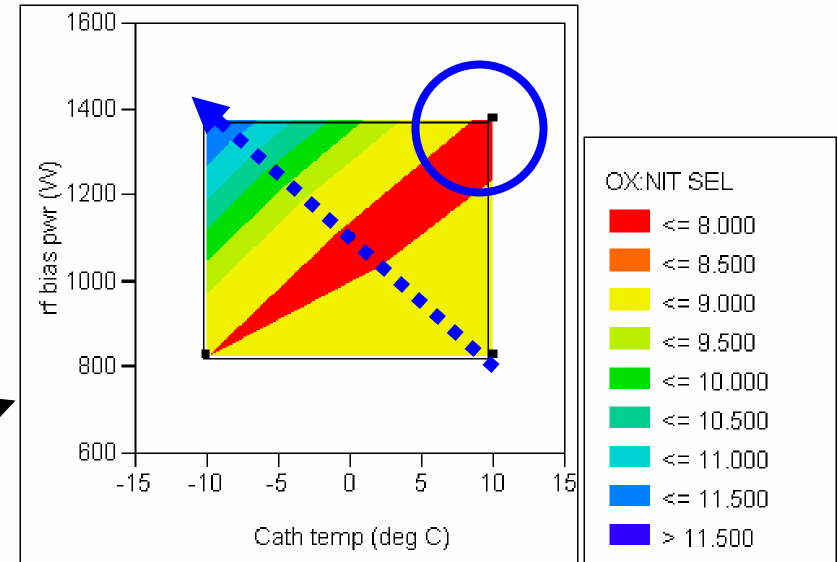
Oxide:Nitride Selectivity Using 1,3-C_4F_6







- ❖ Above 1300 W, Oxide ER is independent of cathode temp.
- ❖ Nitride has non-linear etch rate behavior.
- ❖ With no compromise to anisotropy an acceptable selectivity of at most 8:1 can be obtained at high power and cathode temp.

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Process Conditions Based on Trade-Offs

Cathode Temp (High)/RF Bias (High)/Pressure (Low)

1,3-C_4F_6 with 90% Ar Using DOE: 1, 1, -1

Etch Parameter	Data Output
Via Profile Slope	87 ^{o}
Oxide-Photoresist Selectivity	5.8:1
Oxide-Nitride Selectivity	7.7:1
Oxide Etch Rate	6315 Å/min
Photoresist Etch Rate	1097 Å/min
Silicon Nitride Etch Rate	820 Å/min

* Based on patterned test wafers with dielectric 1

$c\text{-}C_4F_8$ vs. $1,3\text{-}C_4F_6$
Saturated vs. Unsaturated

Etch Parameters	$1,3\text{-}C_4F_6$-Optimized	$c\text{-}C_4F_8$-Optimized	Improvement of $1,3\text{-}C_4F_6$ over $c\text{-}C_4F_8$
PR ER (Å/min)	1831	2563	29%
Ox ER (Å/min)	11204	6815	64%
Nit ER (Å/min)	820	1058	22%
Ox:PR SEL	6:1	3:1	100%
Ox:Nit SEL	13.7:1	6.4:1	114%
Via Profile Slope (°)	89	85.5	4%

$1,3\text{-}C_4F_6$ etch performance is more favorable than $c\text{-}C_4F_8$

* Based on patterned test wafers with dielectric 2

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Etch Performance (ARDE) vs. Plasma Chemistry

Via-hole diameter= 0.273 µm

d(via depth) =0---etch stop initiated

dt

Ion-enhanced Etch Regime

Via Depth_C4F8

Via Depth_C4F6

1.4 1.2 1.0 0.8 0.6 0.4 0.2 0.0

5.1 4.4 3.7 2.9 2.2 1.5 0.7 0.0

0 0.5 1 1.5 2 2.5 3 3.5

Time (min)

ARDE Model-Based Method (i.e., RIE Lag) (Joubert, 1994)

Modulated Etch Time= E_T= [Oxide Target Thickness (Å)]/[Oxide ER (Å/min)]

>>>>>>>>>>>>Polymer build up grossly impedes oxide etching over time

Via Depth

Polymer

E_T=t_o E_T =t_o+ Δt E_T =t_o+ 2Δt E_T =t_o+ 3Δt E_T =t_o+ t∞

Fluorocarbon polymer builds up with increasing etch time.
∴ Plasma chemistry performance at the wafer substrate becomes critical.

- ❖Etch rate is much faster between 0-1.5 min for C_4F_6 than C_4F_8.
- ❖At 1.5 min etch stop is initiated and critical AR is defined.
- ❖ At this point, it is believed that the oxide ER transitions to the fluorocarbon suppression regime.
- ❖ Ion energy flux drops and the oxide etch eventually leads to permanent etch stop.
- ❖**Critical Aspect Ratio is improved by 11.4% for C_4F_6.**

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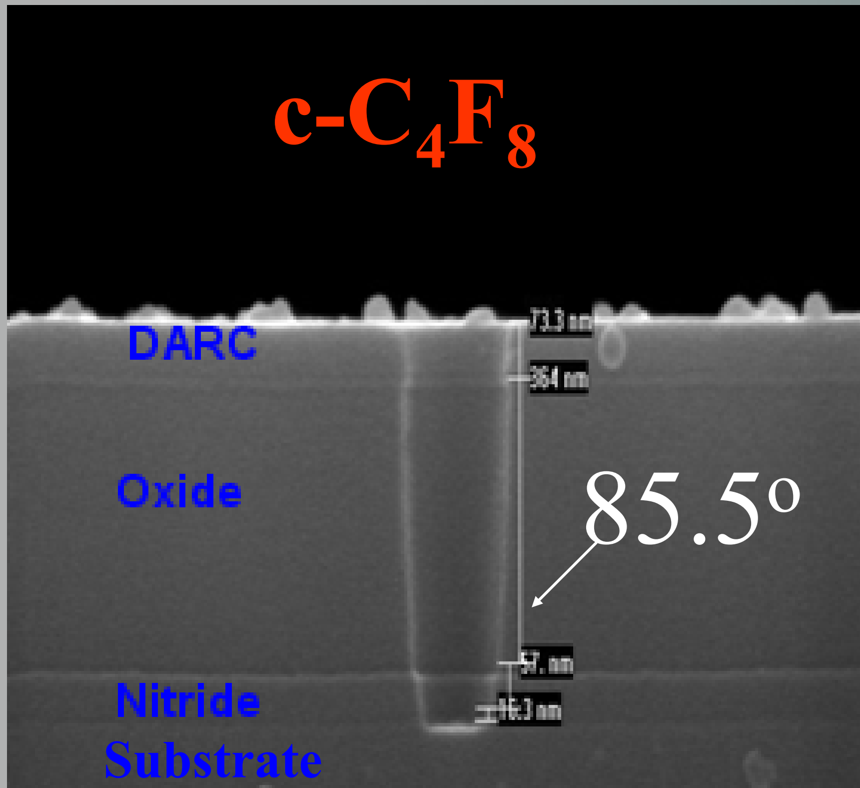
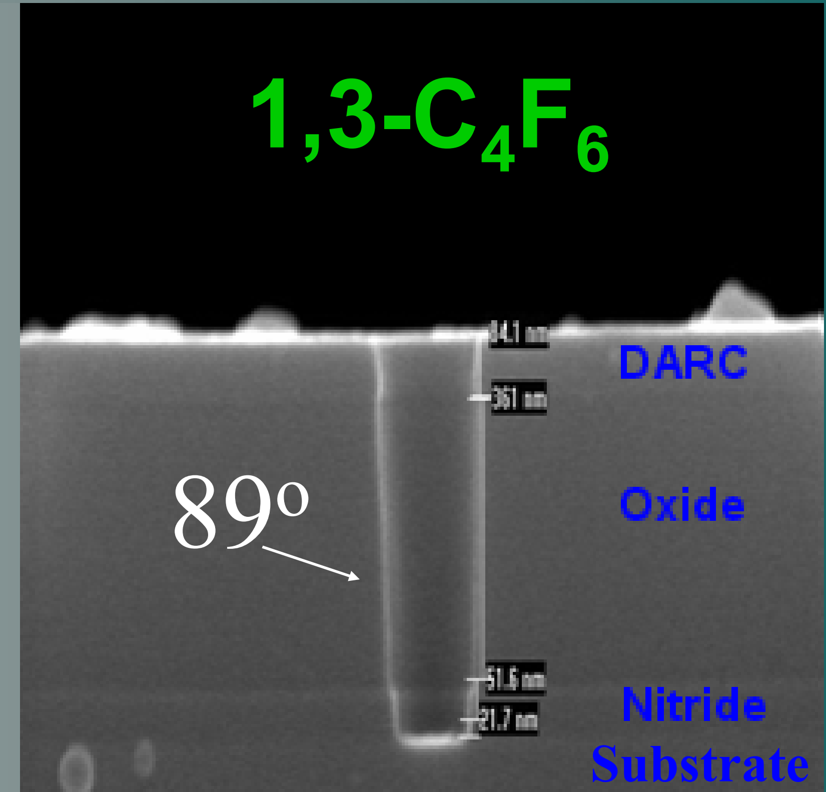
Via Profile vs. Plasma Chemistry





Profile slope shows improvement with 1,3-C_4F_6

* Based on full stack wafers

- The transition from saturated to unsaturated PFC gases display promise in improving the etch performance for increasing aspect ratios.

- Data results showed 1,3-C_4F_6 to increase the oxide-photoresist selectivity by 2 to 1 and the oxide-nitride selectivity by nearly the same. The via profile slope was enhanced (89°) when using 1,3-C_4F_6. Aspect ratio dependent etch (ARDE) was favorably reduced due to the intrinsic characteristics of 1,3-C_4F_6 and optimized process conditions.

- This research addressed a possible resolution to the complexities associated with scaling high-aspect-ratios in via structures. Hexafluorobutadiene (1,3-C_4F_6) is being proposed as an alternative gas to octafluorocyclobutane (c-C_4F_8) in a high-density inductively coupled plasma system.

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