Non-PFC Plasma Chemistries for Patterning Complex Materials/Structures

(*Task Number: 425.038*)

PIs:

- **Jane P. Chang, Chemical and Biomolecular Engineering, UCLA**

Graduate Students:

- **Jack Chen, PhD student, Chemical and Biomolecular Engineering, UCLA**
- **Nicholas Altieri, PhD student, Chemical and Biomolecular Engineering, UCLA**

Other Researchers:

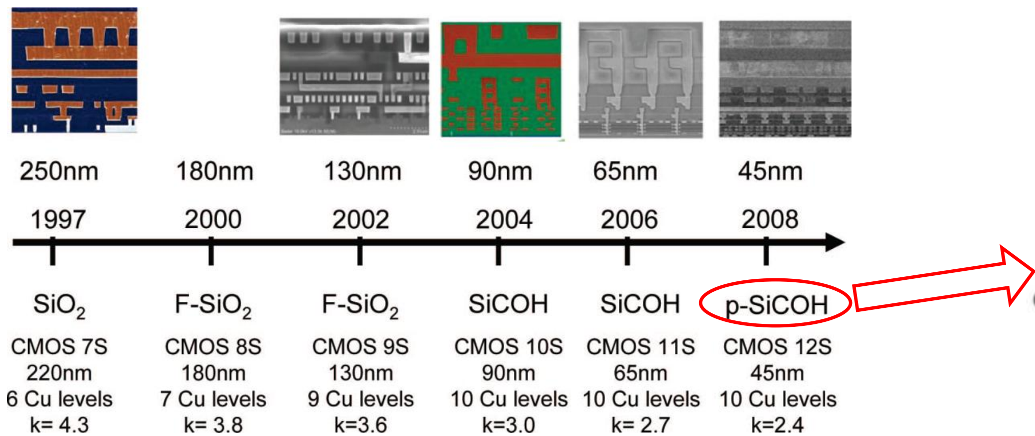
- **Taeseung Kim, postdoc, Chemical and Biomolecular Engineering, UCLA**
- **Michael Paine, undergraduate, Chemical and Biomolecular Engineering, UCLA**

Objectives

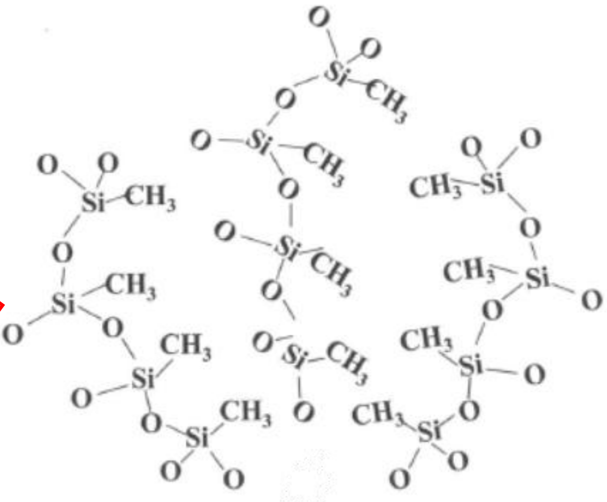
- **Assess the feasibility of non-PFC chemistries in patterning etch-resistant materials (complex materials and structures)**
- **Identify non-PFC alternatives for the etching of carbon doped silica**
- **Examine the use of bond and group additivity methods to determine thermodynamic properties of carbon doped silica**
- **Screen the candidates of chemistries by comparing the pressure of primary etch product in the volatility diagram**

Composition of Low-k Dielectrics[1]

Dielectric materials used in IBM CMOS microprocessors as feature sizes decrease.[2]



Porous carbon-doped silica, a promising low-k dielectric.



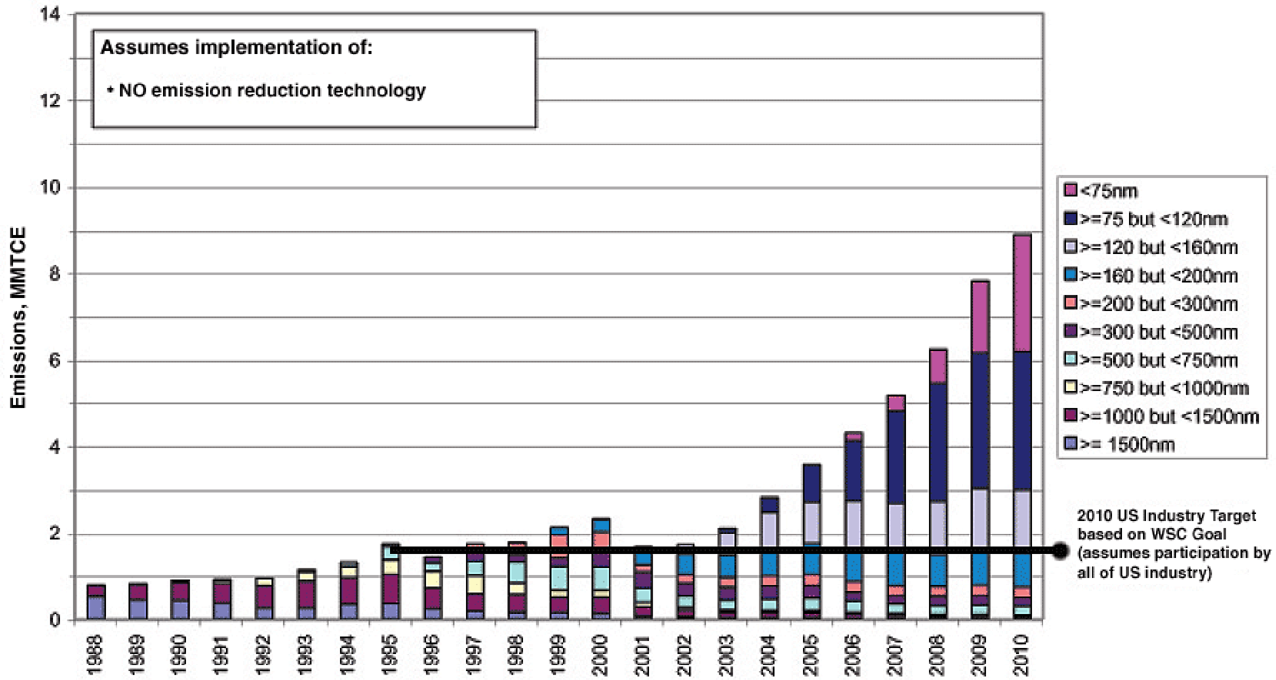
- Introduction of –CH_3 groups lowers the dielectric constant by replacing Si-O bonds with less polarizable Si-C and C-H bonds
- Porosity incorporates air (k = 1) into the film, thereby realizing a lower dielectric constant

[1] Vasarla, 2012 [2] W. Volksen, 2010

PFC Usage in BEOL

US EPA's PFC emission model shows an average PFC emissions from semiconductor manufacturing for the evolution of complex devices[17]

MMTCE= Million metric tons of carbon



- Perfluorocarbon gases are used in BEOL for two major plasma processes: wafer patterning of thin films, especially dielectric films, and the in-situ cleaning of PECVD chambers

[17] PFC reduction/Climate partnership for the semiconductor industry, US EPA (U.S. Environmental Protection Agency), (2008); [18] W. Worth, PFC Technical Update Session, SEMICON/WEST(1995)

Global Warming Potential

Chemistries	Atmospheric conc. in 2005 (ppt)	Con. since 1994* & 1998 (ppt)	Annual emission in late 1990s (Gg)	Radiative efficiency ($W/m^2/ppb$)	Lifetime (year)	Global Warming Potential	Ref.
CO_2	278×10^6	358×10^6*	-	-	variable	1	[12]
CH_4	7×10^5	1721×10^3*	-	-	12.2	21	[12]
N_2O	275×10^3	311×10^3*	-	-	120	310	[12]
$CHClF_2$	-	105×10^3*	-	-	12.1	1400	[12]
CF_4	74	-	~15	0.1	50,000	6500	[13]
CCl_2F_2	-	503×10^3*	-	-	102	7100	[12]
C_2F_6	2.9	3.4	~2	0.26	10,000	9200	[13]
CHF_3	18	22	~7	0.19	270	11700	[12]
SF_6	5.6	7.1	~6	0.52	3,200	23900	[13]
NH_3	-	-	0.054	-	2 hrs	0	[14]
NF_3	<0.1	-	~2.3	0.21	740	16800	[13]
C_2F_4	-	-	-	-	1.9 days	<1	[15]
CF_3I	-	-	-	-	2 days	1	[10]
C_6F_6	-	-	-	-	-	<1	[16]

→ GWP is a simplified index based upon radiative properties that estimates the potential impacts of gases on global warming

Target of Carbon-doped SiO_2 Etch

***Material Metrics as Specified by Intel (Dr. Suri)**

Intel specified metrics:

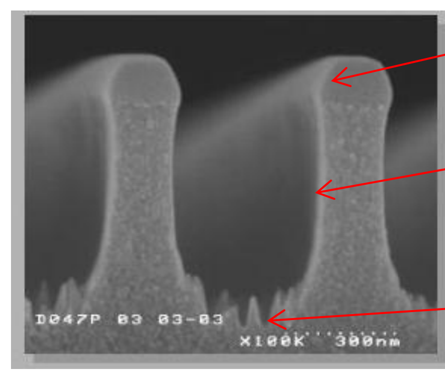
Elements	Range(%)
Si	20%
O	40%
C	15-40%
Porosity	20-25%
Thickness	100nm

Focus on:

1	Trench etch (later via)
2	Selectivity to PR
3	Sidewall damage

Target	Carbon doping level	Composition Si (%)	O (%)	C (%)	H (%)	Unit
1	Low	15.4	23.1	15.4	46.1	$SiO_{1.5}CH_3$
2		20	20	20	40	$SiOCH_2$
3		12.5	12.5	25	50	$SiO(CH_2)_2$
4	High	18.2	27.2	36.4	18.2	$SiO_{1.5}C_2H$

- SEM of C-doped SiO_2 etch by CF_4/Ar [a]



[a] Etching of high k dielectrics, Plasma Technology for Advanced Devices, 2006, http://clarycon.blogspot.com/2006/12/etching-of-high-k-dielectrics.html

Systematic Approach - Thermodynamic

- Thermodynamic approach can be systematic
  - If such data is available
    - NIST-JANAF Thermo-chemical tables
    - HSC Chemistry for windows, chemical reaction and equilibrium software with extensive thermo-chemical database
    - FACT, Facility for Analysis of Chemical Thermodynamics
    - Barin and Knacke tables (thermo-chemical data for pure substances and inorganic substances)
  - Determination of dominant surface/gas-phase species
  - Assessment of possible reactions

- Graphical Representation of thermodynamic analysis
  - Richardson Ellingham diagram
  - Pourbaix diagram
  - Volatility diagram

Effect of Doping

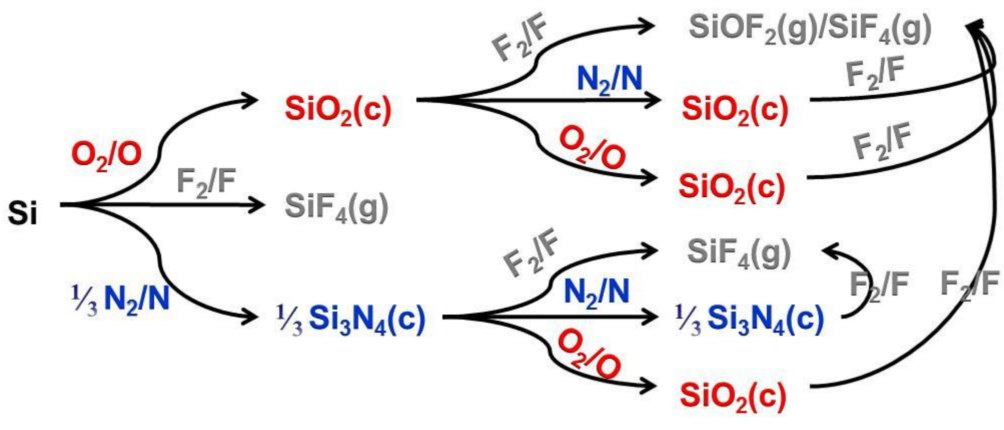
Gas phase

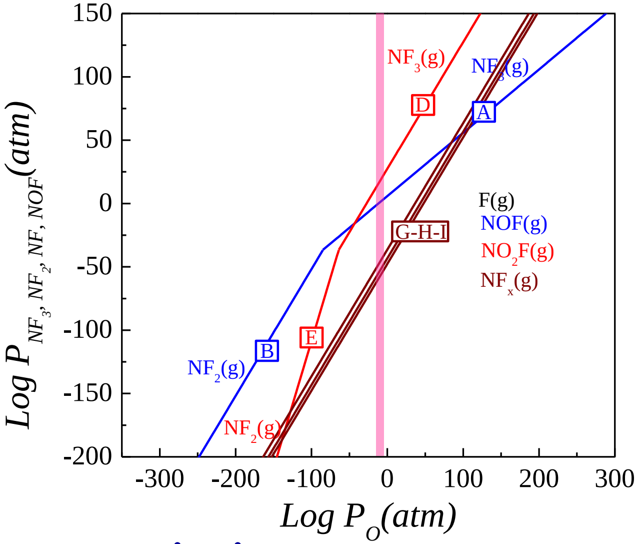
	NF$_3$ with Oxygen-300K	G(eV)	log(K)
A	$O(g) + NF_3(g) \rightarrow NOF(g) + 2F(g)$	-0.70	11.7
B	$O(g) + NF_2(g) \rightarrow NOF(g) + F(g)$	-2.87	48.1
C	$O(g) + NF(g) \rightarrow NOF(g)$	-5.45	91.5
D	$2O(g) + NF_3(g) \rightarrow NO_2F(g) + 2F(g)$	-3.26	54.8
E	$2O(g) + NF_2(g) \rightarrow NO_2F(g) + F(g)$	-5.43	91.3
F	$2O(g) + NF(g) \rightarrow NO_2F(g)$	-8.01	134.6

	NF$_3$-300K	G(eV)	log(K)
G	$NF_3(g) \rightarrow NF_2(g) + F(g)$	2.17	-36.4
H	$NF_2(g) \rightarrow NF(g) + F(g)$	2.58	-43.3
I	$NF(g) \rightarrow N(g) + F(g)$	2.84	-47.7

Surface

	Si$_3$N$_4$-O$_2$-F-300K	G(eV)	log(K)
1	$Si(c) + \frac{1}{2}O_2\ (g) \rightarrow SiO(g)$	-1.32	22.0
2	$SiO_2\ (c) \rightarrow SiO(g) + \frac{1}{2}O_2\ (g)$	7.56	-126.5
3	$\frac{1}{2}Si_2N_2O(c) \rightarrow Si(c) + \frac{1}{2}N_2\ (g) + \frac{1}{4}O_2\ (g)$	4.47	75.0
4	$\frac{1}{2}Si_2N_2O(c) + \frac{3}{4}O_2\ (g) \rightarrow SiO_2(c) + \frac{1}{2}N_2\ (g)$	-4.41	74.0
5	$\frac{1}{2}Si_2N_2O(c) + \frac{1}{4}O_2\ (g) \rightarrow SiO(g) + \frac{1}{2}N_2\ (g)$	3.15	-52.5
15	$SiO_2(c) + 4F(g) \rightarrow SiF_4(g) + O_2\ (g)$	-10.00	168.0
16	$SiO_2(c) + 2F(g) \rightarrow SiF_2(g) + O_2\ (g)$	1.39	-23.0
21	$\frac{1}{3}Si_3N_4(c) + \frac{1}{2}O_2\ (g) \rightarrow SiO(g) + \frac{2}{3}N_2(g)$	0.90	-15.0
22	$\frac{1}{3}Si_3N_4(c) + \frac{1}{4}O_2\ (g) \rightarrow \frac{1}{2}Si_2N_2O(c) + \frac{1}{6}N_2\ (g)$	-2.25	37.7



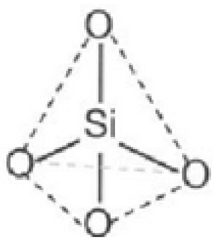
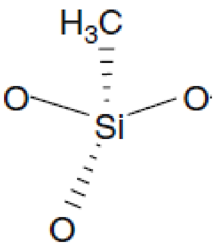
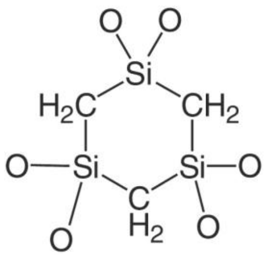
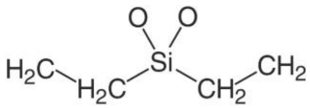
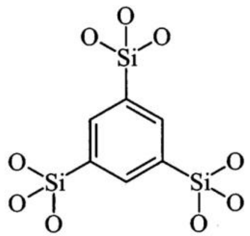


- Doping changes the etching characteristics

SRC Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

[4] NIST-JANAF Thermochemical (2013)

Data for C-doped Silica is Limited

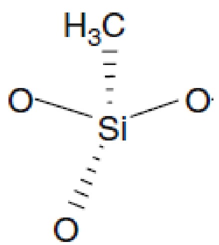
C-doped Silica	SiO_2[4]	$SiO_{1.5}CH_3$[4,5] (15.4%)	$SiOCH_2$[4,5] (20%)	$SiO(CH_2)_2$[4,5] (25%)	$SiO_{1.5}C_2H$[4,5,6] (36.4%)
Molecular Structure					
$\Delta_f H$ (kJ/mol)	-910.87				
$\Delta_f S$ (J/mol)	-182.53		No data is available		
$\Delta_f G$ (kJ/mol)	-856.11				

- The thermodynamic data of C-doped silica is not available in NIST, HSC chemistry and Perry's handbook

[4] NIST-JANAF Thermochemical (2013)

Bond and Group Additivity Method

- The bond additivity and group additivity methods proposed by Benson and Buss[3], is used to determine the energy of formation for C-doped silica
- Test case of one unit $SiO_{1.5}CH_3$ (15.4%)



$$\Delta_f S_{carbon-doped\ SiO_2} = S^\circ_{carbon-doped\ SiO_2} - (nS^\circ_{Si} + xS^\circ_{O_2} + yS^\circ_{C} + zS^\circ_{H_2})$$

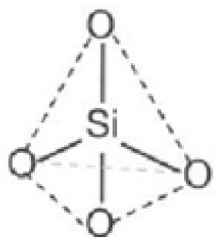
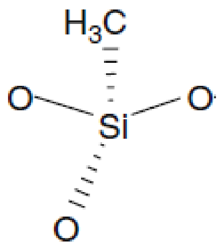
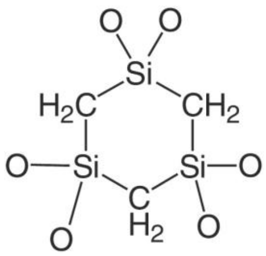
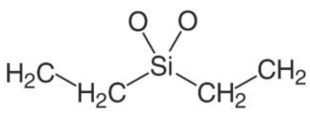
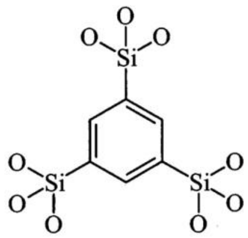
$$\Delta_f G_{carbon-doped\ SiO_2} = \Delta_f H_{carbon-doped\ SiO_2} - T \times \Delta_f S_{carbon-doped\ SiO_2}$$

Group / Bond	No. in $SiO_{1.5}CH_3$	Enthalpy[5] (kJ/mol)	Entropy[5] (J/mol*K)
SiO_2[6]	3/4	-910.9	-
CH_4[6]	3/4	-50.6	-
Si-C	1	-25.1	57.9
Si-O	3	-	-5.2
C-H	3	-	54.0
Total	-	-746.2	204.3

T=300K	SiO_2[4]	$SiO_{1.5}CH_3$
$\Delta_f H$(kJ/mol)	-910.9	-746.2
$\Delta_f S$(J/mol)	-182.5	-324.8
$\Delta_f G$(kJ/mol)	-856.1	-648.8

[3] S. W. Benson, ACS Symposium series 677, (1988) [4] NIST-JANAF Thermochemical (2013)

Compare ΔG for C-doped Silica

C-doped Silica	SiO_2[4]	$SiO_{1.5}CH_3$[4,5] (15.4%)	$SiOCH_2$[4,5] (20%)	$SiO(CH_2)_2$[4,5] (25%)	$SiO_{1.5}C_2H$[4,5,6] (36.4%)
Molecular Structure					
$\Delta_f H$ (kJ/mol)	-910.87	-746.20	-517.40	-538.00	-662.70
$\Delta_f S$ (J/mol)	-182.53	-324.77	-44.88	-141.84	-328.86
$\Delta_f G$ (kJ/mol)	-856.11	-648.80	-503.90	-495.50	-564.10

- Compounds with fewer Si-O bonds are more readily etched

[4] NIST-JANAF Thermochemical (2013)

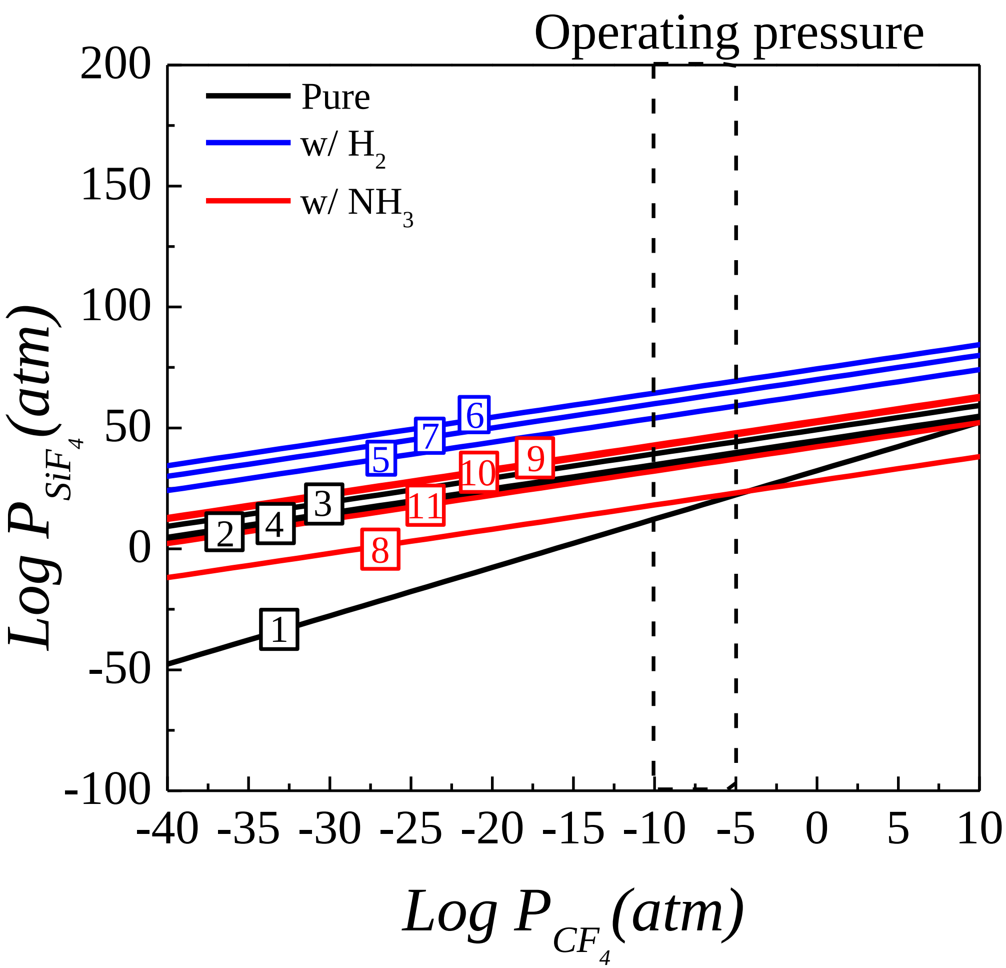
Selection of Chemistry

- Comparison of non-PFC and PFC in C-doped silica etch
- Consider the additives such as H_2 and NH_3 to facilitate the formation of volatile C-containing compounds from highly-doped silica (>15%C)

Reaction	ΔG (eV)
SiO_2	
$SiO_2(c)$ + **$2CF_4(g)$** → $SiF_4(g) + 2COF_2(g)$	-1.92
$SiO_2(c)$ + **$2CF_4(g)$** + **$H_2(g)$** → $SiF_4(g) + 2COF(g) + 2HF(g)$	1.51
$SiO_2(c)$ + **$2CF_4(g)$** + **$NH_3(g)$** → $SiF_4(g) + COF_2(g) + HCN(g) + HOF(g) + HF(g)$	3.03
$SiO(CH_2)_2(c)$ (25%C-doped silica)	
$SiO(CH_2)_2(c)$ + **$CF_4(g)$** → $SiF_4(g) + CO(g) + C_2H_4(g)$	-2.67
$SiO(CH_2)_2(c)$ + **$CF_4(g)$** + 2**H_2**(g) → $SiF_4(g) + CO(g) + 2CH_4(g)$	-4.43
$SiO(CH_2)_2(c)$ + **$CF_4(g)$** + **$2/3NH_3(g)$** → $SiF_4(g) + CO(g) + 2/3HCN(g) + 4/3CH_4(g)$	-3.10

[4] NIST-JANAF Thermochemical (2013)

Etching with CF_4

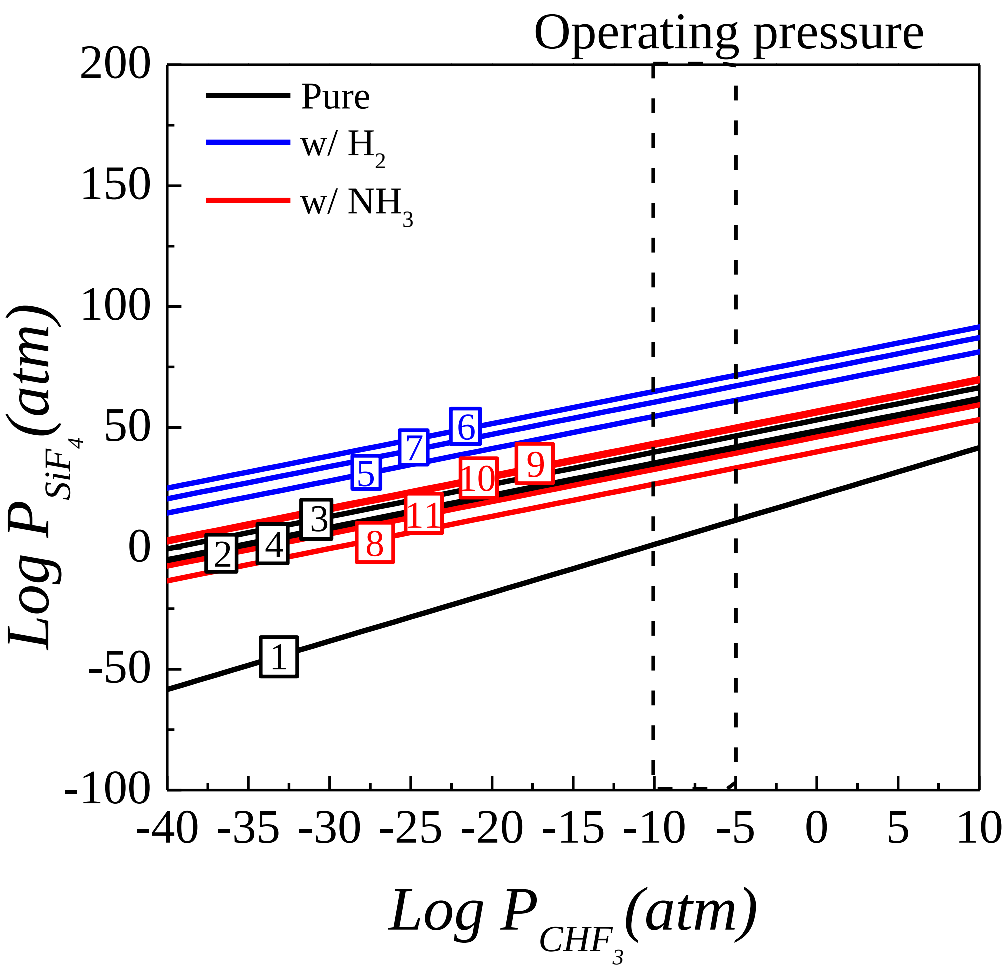


	Reaction	G (eV) [4,5,6]
[1]	**SiO_2**(c) + $2CF_4$(g) → SiF_4(g) + $2COF_2$(g)	-1.92
[2]	2**$SiO_{1.5}CH_3$**(c) + $2CF_4$(g) → $2SiF_4$(g) + COH_2(g) + CH_4(g) + 2CO(g)	-5.24
[3]	2**$SiOCH_2$**(c) + $2CF_4$(g) → $2SiF_4$(g) + C_2H_4(g) + 2CO(g)	-5.87
[4]	**$SiO(CH_2)_2$**(c) + CF_4(g) → SiF_4(g) + CO(g) + C_2H_4(g)	-2.67
[5]	**$SiOCH_2$**(c) + CF_4(g) + **H_2**(g) → SiF_4(g) + CO(g) + CH_4(g)	-3.82
[6]	**$SiO(CH_2)_2$**(c) + CF_4(g) + 2**H_2**(g) → SiF_4(g) + CO(g) + $2CH_4$(g)	-4.43
[7]	2**$SiO_{1.5}C_2H$**(c) + $2CF_4$(g) + 5**H_2**(g) → $2SiF_4$(g) + 3CO(g) + $3CH_4$(g)	-8.33
[8]	6**$SiO_{1.5}CH_3$**(c) + $6CF_4$(g) + **NH_3**(g) → $6SiF_4$(g) + HCN(g) + $6COH_2$(g) + $2CH_4$(g) + 3CO(g)	-12.88
[9]	3**$SiOCH_2$**(c) + $3CF_4$(g) + **NH_3**(g) → $3SiF_4$(g) + 3CO(g) + HCN(g) + $2CH_4$(g)	-9.46
[10]	3**$SiO(CH_2)_2$**(c) + $3CF_4$(g) + 2**NH_3**(g) → $3SiF_4$(g) + 3CO(g) + 2HCN(g) + $4CH_4$(g)	-9.31
[11]	6**$SiO_{1.5}C_2H$**(c) + $6CF_4$(g) + 5**NH_3**(g) → $6SiF_4$(g) + 9CO(g) + 5HCN(g) + $4CH_4$(g)	-15.07

- H_2 addition increases the etch product pressure – most effective with 25% C-doped silica
- NH_3 addition has little effect – most effective with 20% C-doped silica

[4] NIST-JANAF Thermochemical (2013)

Etching with CHF_3

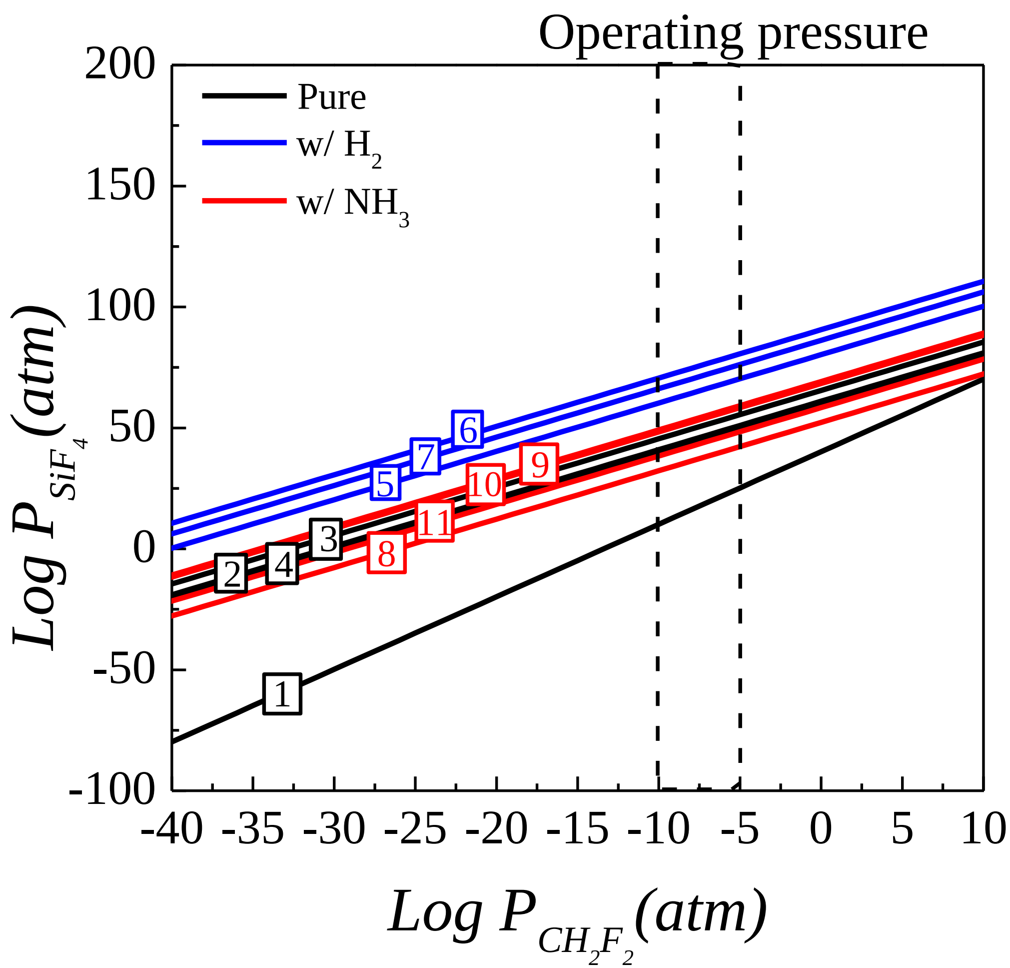


	Reaction	G (eV) [4,5,6]
[1]	$SiO_2(c) + 2CHF_3(g) \rightarrow COF_2(g) + SiF_4(g) + COH_2(g)$	-1.29
[2]	$6SiO_{1.5}CH3(c) + 8CHF_3(g) \rightarrow 6SiF_4(g) + 3COH_2(g) + 5CH_4(g) + 6CO(g)$	-17.09
[3]	$6SiOCH_2(c) + 8CHF_3(g) \rightarrow 6SiF_4(g) + 6CO(g) + 3C_2H_4(g) + 2CH_4(g)$	-18.97
[4]	$3SiO(CH_2)_2(c) + 4CHF_3(g) \rightarrow 3SiF_4(g) + 3CO(g) + CH_4(g) + 3C_2H_4(g)$	-8.68
[5]	$3SiOCH_2(c) + 4CHF_3(g) + 3H_2(g) \rightarrow 3SiF_4(g) + 3CO + 4CH_4(g)$	-12.13
[6]	$3SiO(CH_2)_2(c) + 4CHF_3(g) + 6H_2(g) \rightarrow 3SiF_4(g) + 3CO(g) + 7CH_4(g)$	-13.97
[7]	$6SiO_{1.5}C_2H(c) + 8CHF_3(g) + 15H_2(g) \rightarrow 6SiF_4(g) + 9CO(g) + 11CH_4(g)$	-26.37
[8]	$6SiO_{1.5}CH_3(c) + 8CHF_3(g) + NH_3(g) \rightarrow 6SiF_4(g) + HCN(g) + 6COH_2(g) + 4CH_4(g) + 3CO(g)$	-14.25
[9]	$3SiOCH_2(c) + 4CHF_3(g) + NH_3(g) \rightarrow 3SiF_4(g) + 3CO(g) + HCN(g) + 3CH_4(g)$	-10.14
[10]	$3SiO(CH_2)_2(c) + 4CHF_3(g) + 2NH_3(g) \rightarrow 3SiF_4(g) + 3CO(g) + 2HCN(g) + 5CH_4(g)$	-10.00
[11]	$6SiO_{1.5}C_2H(c) + 8CHF_3(g) + 5NH_3(g) \rightarrow 6SiF_4(g) + 9CO(g) + 5HCN(g) + 6CH_4(g)$	-16.43

- H_2 addition increases the etch product pressure – most effective with 25% C-doped silica
- NH_3 addition has little effect – most effective with 20% C-doped silica

[4] NIST-JANAF Thermochemical (2013)

Etching with CH_2F_2



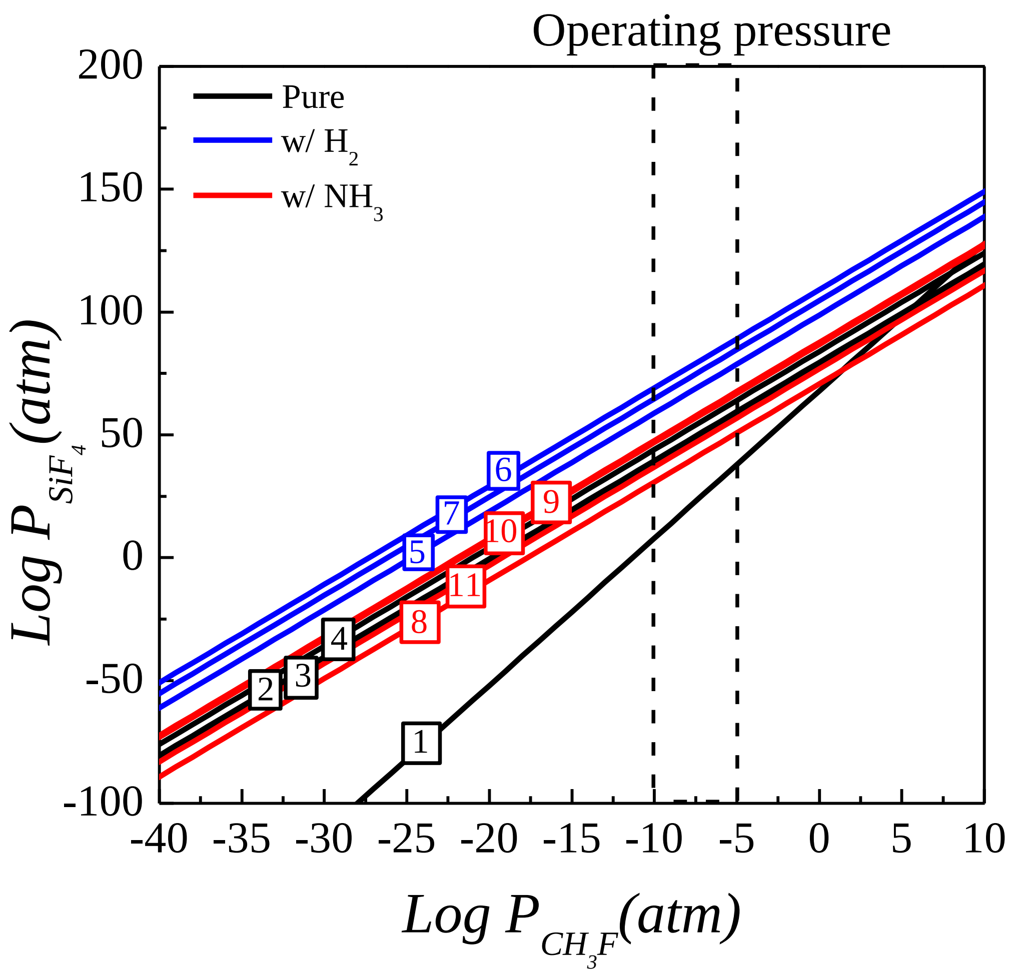
	Reaction	G (eV) [4,5,6]
[1]	$\mathbf{SiO_2}$(c) + $3CH_2F_2$(g) → COF_2(g) + SiF_4(g) + COH_2(g) + CH_4(g)	-2.39
[2]	2$\mathbf{SiO_{1.5}CH_3}$(c) + $4CH_2F_2$(g) → $2SiF_4$(g) + COH_2(g) + 2CO(g) + $3CH_4$(g)	-7.17
[3]	2$\mathbf{SiOCH_2}$(c) + $4CH_2F_2$(g) → $2SiF_4$(g) + 2CO(g) + C_2H_4(g) + $2CH_4$(g)	-7.80
[4]	$\mathbf{SiO(CH_2)_2}$(c) + $2CH_2F_2$(g) → SiF_4(g) + CO(g) + C_2H_4(g) + CH_4(g)	-3.63
[5]	$\mathbf{SiOCH_2}$(c) + $2CH_2F_2$(g) + $\mathbf{H_2}$(g) → SiF_4(g) + CO(g) + $2CH_4$(g)	-4.78
[6]	$\mathbf{SiO(CH_2)_2}$(c) + $2CH_2F_2$(g) + 2$\mathbf{H_2}$(g) → SiF_4(g) + CO(g) + $3CH_4$(g)	-5.39
[7]	2$\mathbf{SiO_{1.5}C_2H}$(c) + $4CH_2F_2$(g) + 5$\mathbf{H_2}$(g) → $2SiF_4$(g) + 3CO(g) + $5CH_4$(g)	-10.26
[8]	6$\mathbf{SiO_{1.5}CH_3}$(c) + $12CH_2F_2$(g) + $\mathbf{NH_3}$(g) → $6SiF_4$(g) + HCN(g) + $6COH_2$(g) + $8CH_4$(g) + 3CO(g)	-18.67
[9]	3$\mathbf{SiOCH_2}$(c) + $6CH_2F_2$(g) + $\mathbf{NH_3}$(g) → $3SiF_4$(g) + 3CO(g) + HCN(g) + $5CH_4$(g)	-12.35
[10]	3$\mathbf{SiO(CH_2)_2}$(c) + $6CH_2F_2$(g) + 2$\mathbf{NH_3}$(g) → $3SiF_4$(g) + 3CO(g) + 2HCN(g) + $7CH_4$(g)	-12.21
[11]	6$\mathbf{SiO_{1.5}C_2H}$(c) + $12CH_2F_2$(g) + 5$\mathbf{NH_3}$(g) → $6SiF_4$(g) + 9CO(g) + 5HCN(g) + $10CH_4$(g)	-20.86

- H_2 addition increases the etch product pressure – most effective with 25% C-doped silica
- NH_3 addition has little effect – most effective with 20% C-doped silica

SRC Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

[4] NIST-JANAF Thermochemical (2013)

Etching with CH_3F

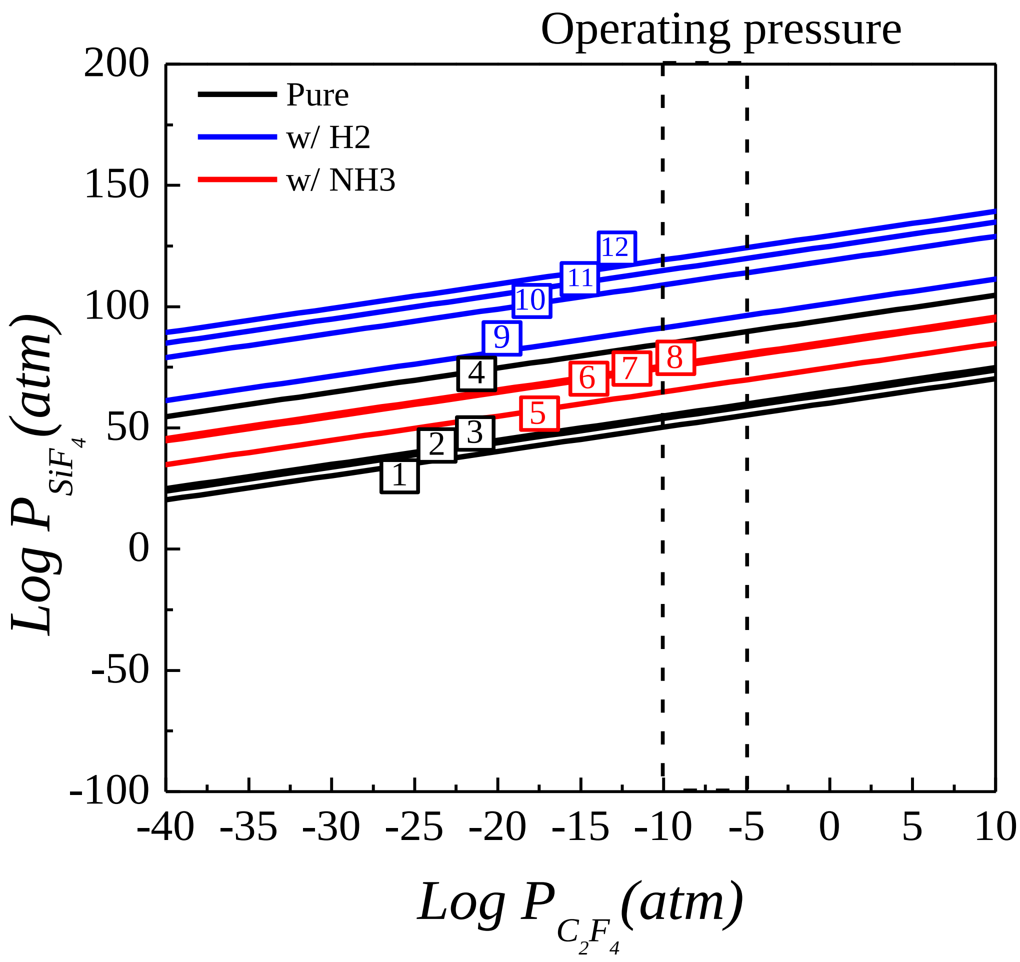


	Reaction	G (eV) [4,5,6]
[1]	SiO_2(c) + 6CH_3F(g)→ COF_2(g) + SiF_4(g) + 4CH4(g) + COH2(g)	-4.04
[2]	2$SiO_{1.5}CH_3$(c) + 8CH_3F(g) → 2SiF_4(g) + 2CO(g) + COH_2(g) + 7CH_4(g)	-9.37
[3]	2$SiOCH_2$(c) + 8CH_3F(g) → 2SiF_4(g) + 2CO(g) + C_2H_4(g) + 6CH_4(g)	-10.00
[4]	$SiO(CH_2)_2$(c) + 4CH_3F(g) → SiF_4(g) + CO(g) + C_2H_4(g) + 3CH_4(g)	-4.73
[5]	$SiOCH_2$(C) + 4CH_3F(g) + H_2(g) → SiF_4(g) + CO(g) + 4CH_4(g)	-5.88
[6]	$SiO(CH_2)_2$(c) + 4CH_3F(g) + 2H_2(g) → SiF_4(g) + CO(g) + 5CH_4(g)	-6.50
[7]	2$SiO_{1.5}C_2H$(c) + 8CH_3F(g) + 5H_2(g) → 2SiF_4(g) + 3CO(g) + 9CH_4(g)	-12.47
[8]	6$SiO_{1.5}CH_3$(c) + 24CH_3F(g) + NH_3(g) → 6SiF_4(g) + HCN(g) + 6COH_2(g) + 20CH_4(g) + 3CO(g)	-25.28
[9]	3$SiOCH_2$(c) + 12CH_3F(g) + NH_3(g) → 3SiF_4(g) + 3CO(g) + HCN(g) + 11CH_4(g)	-15.66
[10]	3$SiO(CH_2)_2$(c) + 12CH_3F(g) + 2NH_3(g) → 3SiF_4(g) + 3CO(g) + 2HCN(g) + 13CH_4(g)	-15.51
[11]	6$SiO_{1.5}C_2H$(c) + 24CH_3F(g) + 5NH_3(g) → 6SiF_4(g) + 9CO(g) + 5HCN(g) + 22CH_4(g)	-27.46

- H_2 addition increases the etch product pressure – most effective with 25% C-doped silica
- NH_3 addition has little effect – most effective with 20% C-doped silica

[4] NIST-JANAF Thermochemical (2013)

Etching with C_2F_4

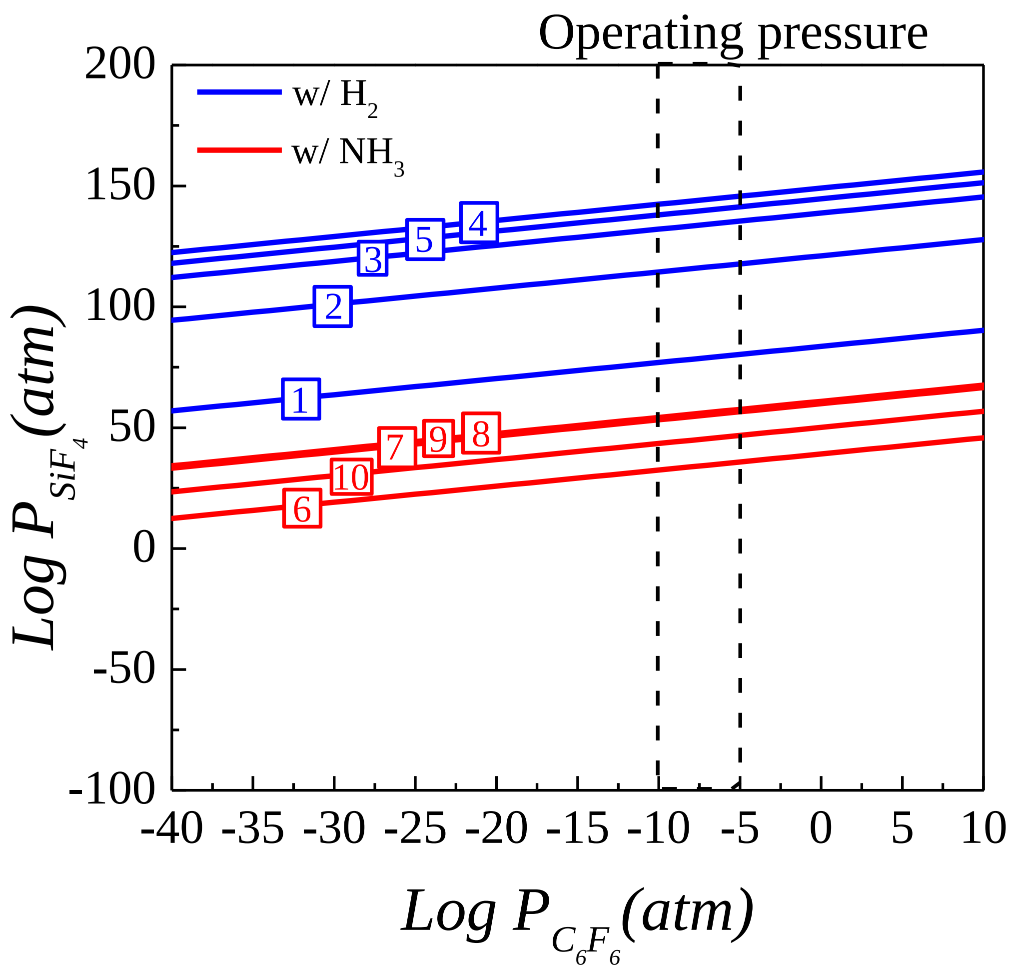


	Reaction	G (eV) [4,5,6]
[1]	2SiO(CH2)2(c) + 2C2F4(g) → 2SiF4(g) + 2CO(g) + C2H4(g) + 2C2H2(g)	-7.18
[2]	SiO2(c) + C2F4(g) → SiF4(g) + 2CO(g)	-3.80
[3]	SiOCH2(c) + C2F4(g) → SiF4(g) + CO(g) + C2H2(g)	-3.87
[4]	4SiO1.5CH3(c) + 4C2F4(g) → 4SiF4(g) + 6CO(g) + 3CH4(g)	-22.55
[5]	2SiO1.5C2H(c) + 2C2F4(g) + 3NH3(g) → 2SiF4(g) + 3CO(g) + 2CH4(g) + 3HCN(g)	-8.91
[6]	2SiO1.5CH3(c) + 2C2F4(g) + NH3(g) → 2SiF4(g) + HCN(g) + 3CO(g) + 2CH4(g)	-10.08
[7]	3SiO(CH2)2(c) + 3C2F4(g) + 4NH3(g) → 3SiF4(g) + 4HCN(g) + 3CO(g) + 5CH4(g)	-15.15
[8]	SiOCH2(c) + C2F4(g) + NH3(g) → SiF4(g) + HCN(g) + CO(g) + CH4(g)	-5.10
[9]	2SiO1.5CH3(c) + 2C2F4(g) + 3H2(g) → 2SiF4(g) + 3CO(g) + 3CH4(g)	-12.06
[10]	SiOCH2(c) + C2F4(g) + 3H2(g) → SiF4(g) + CO(g) + 2CH4(g)	-7.08
[11]	2SiO1.5C2H(c) + 2C2F4(g) + 9H2(g) → 2SiF4(g) + 3CO(g) + 5CH4(g)	-14.87
[12]	SiO(CH2)2(c) + C2F4(g) + 4H2(g)→ SiF4(g) + CO(g) + 3CH4(g)	-7.70

- All chemistries are most effective with 36.4% C-doped silica

[4] NIST-JANAF Thermochemical (2013)

Etching with C_6F_6

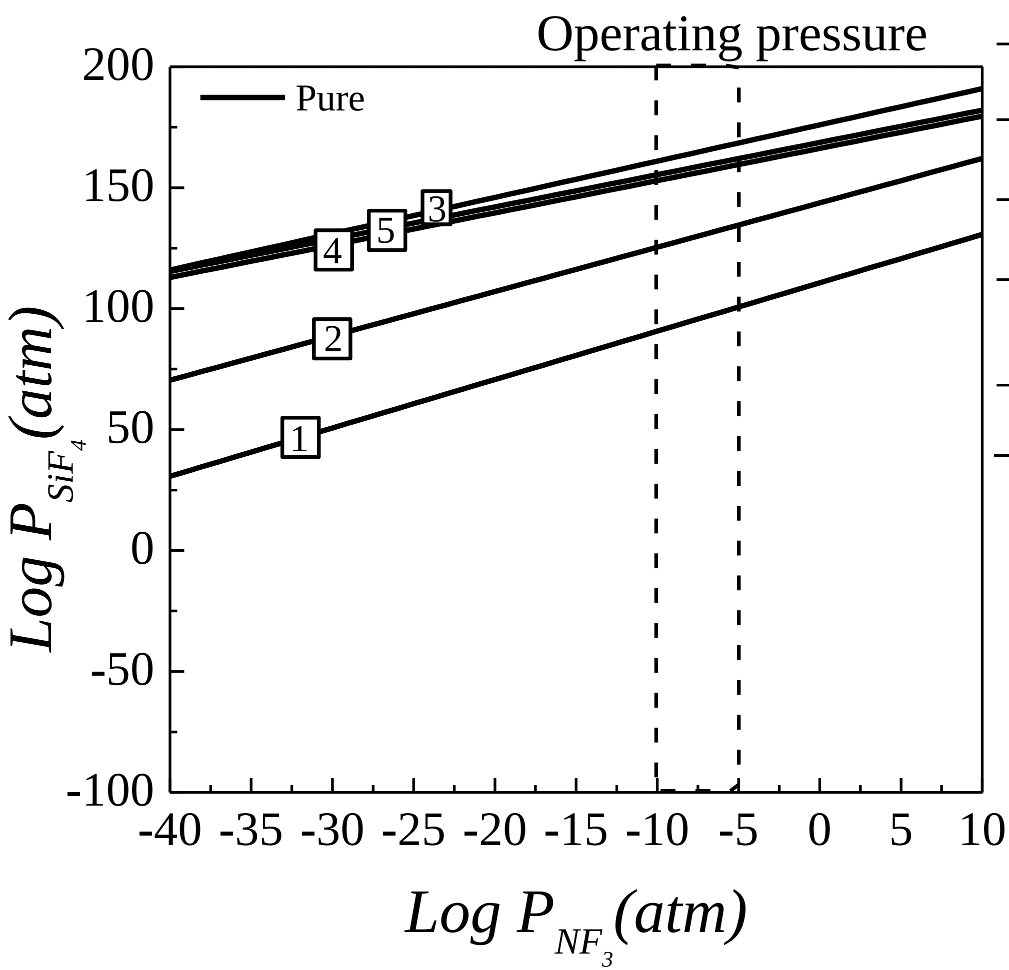


	Reaction	G (eV) [4,5,6]
[1]	$3\mathbf{SiO_2}$(c) + $2C_6F_6$(g) + $12\mathbf{H_2}$(g) → $3SiF_4$(g) + 6CO(g) + $6CH_4$(g)	-14.94
[2]	$6\mathbf{SiO_{1.5}CH_3}$(c) + $4C_6F_6$(g) + $33\mathbf{H_2}$(g) → $6SiF_4$(g) + 9CO(g) + $21CH_4$(g)	-43.25
[3]	$3\mathbf{SiOCH_2}$(c) + $2C_6F_6$(g) + $21\mathbf{H_2}$(g) → $3SiF_4$(g) + 3CO(g) + $12CH_4$(g)	-24.78
[4]	$3\mathbf{SiO(CH_2)_2}$(c) + $2C_6F_6$(g) + $24\mathbf{H_2}$(g) → $3SiF_4$(g) + 3CO(g) + $15CH_4$(g)	-26.63
[5]	$6\mathbf{SiO_{1.5}C_2H}$(c) + $4C_6F_6$(g) + $51\mathbf{H_2}$(g) → $6SiF_4$(g) + 9CO(g) + $27CH_4$(g)	-51.68
[6]	$3\mathbf{SiO_2}$(c) + $2C_6F_6$(g) + $4\mathbf{NH_3}$(g) → $3SiF_4$(g) + 6CO(g) + 4HCN(g) + $2CH_4$(g)	-6.99
[7]	$6\mathbf{SiO_{1.5}CH_3}$(c) + $4C_6F_6$(g) + $11\mathbf{NH_3}$(g) → $6SiF_4$(g) + 9CO(g) + 11HCN(g) + $10CH_4$(g)	-21.40
[8]	$3\mathbf{SiOCH_2}$(c) + $2C_6F_6$(g) + $7\mathbf{NH_3}$(g) → $3SiF_4$(g) + 3CO(g) + 7HCN(g) + $5CH_4$(g)	-10.88
[9]	$3\mathbf{SiO(CH_2)_2}$(c) + $2C_6F_6$(g) + $8\mathbf{NH_3}$(g) → $3SiF_4$(g) + 3CO(g) + 8HCN(g) + $7CH_4$(g)	-10.73
[10]	$6\mathbf{SiO_{1.5}C_2H}$(c) + $4C_6F_6$(g) + $17\mathbf{NH_3}$(g) → $6SiF_4$(g) + 9CO(g) + 17HCN(g) + $10CH_4$(g)	-17.91

- H_2 addition increases the etch product pressure – most effective with 25% C-doped silica
- NH_3 increases the etch product pressure – most effective with 15.4% C-doped silica

[4] NIST-JANAF Thermochemical (2013)

Etching with NF_3



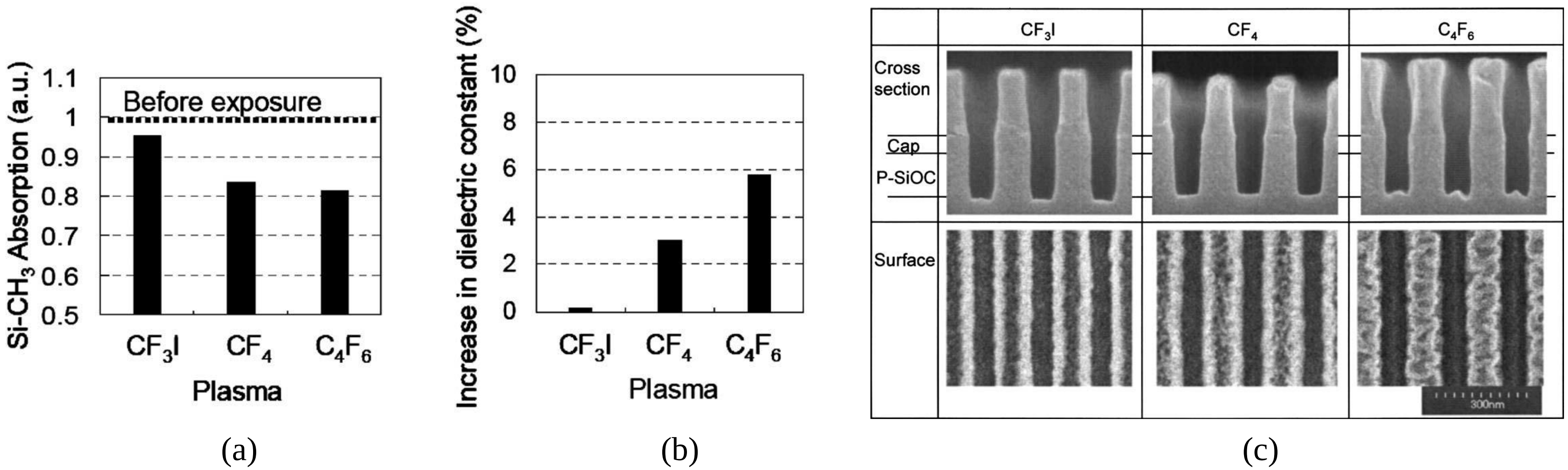
	Reaction	G (eV) [4,5,6]
[1]	$\mathbf{SiO_2}$(c) + 2NF_3(g) → SiF_4(g) + 2NOF(g)	-6.59
[2]	6$\mathbf{SiO_{1.5}CH_3}$(c) + 11NF_3(g) → 6SiF4(g) + 9NOF(g) + 2HCN(g) + 4CH4(g)	-51.34
[3]	2$\mathbf{SiOCH_2}$(c) + 3NF_3(g) → 2SiF_4(g) + HF(g) + HCN(g) + COH_2(g) + N_2O(g)	-20.95
[4]	3$\mathbf{SiO(CH_2)_2}$(c) + 4NF_3(g) → 3SiF_4(g) + 2HCN(g) + CO(g) + COH_2(g) + N_2O(g) + 2CH_4(g)	-29.69
[5]	6$\mathbf{SiO_{1.5}C_2H}$(c) + 8NF_3(g) → 6SiF_4(g) + 6HCN(g) + N_2O(g) + 2CO_2(g) + 4CO(g)	-60.27

- $NF_{3\ is}$ most effective with 20% C-doped silica

Low Damage Etching with CF_3I[8]

Etchant	Etch Rate (nm/min)	GWP
CF_3I	250	1
CF_4	200	6500
C_4F_6	410	290

- CF_3I produces less UV radiation
- I atoms scavenge F radicals to form IF_x
- Less damage to doped carbon keeps dielectric constant low



(a) Decrease in absorption corresponding to $Si\text{-}CH_3$ bond. (b) Increase in dielectric constant after etching. (c) Etch profiles of porous SiOCH.

[8] Eiichi Soda, et al. J. Vac. Sci. Tech. A 26, 875 (2008) – from Semiconductor Leading Edge Technologies, Inc., Japan & Tohoku University, Japan

Environmental Impact of CF_3I

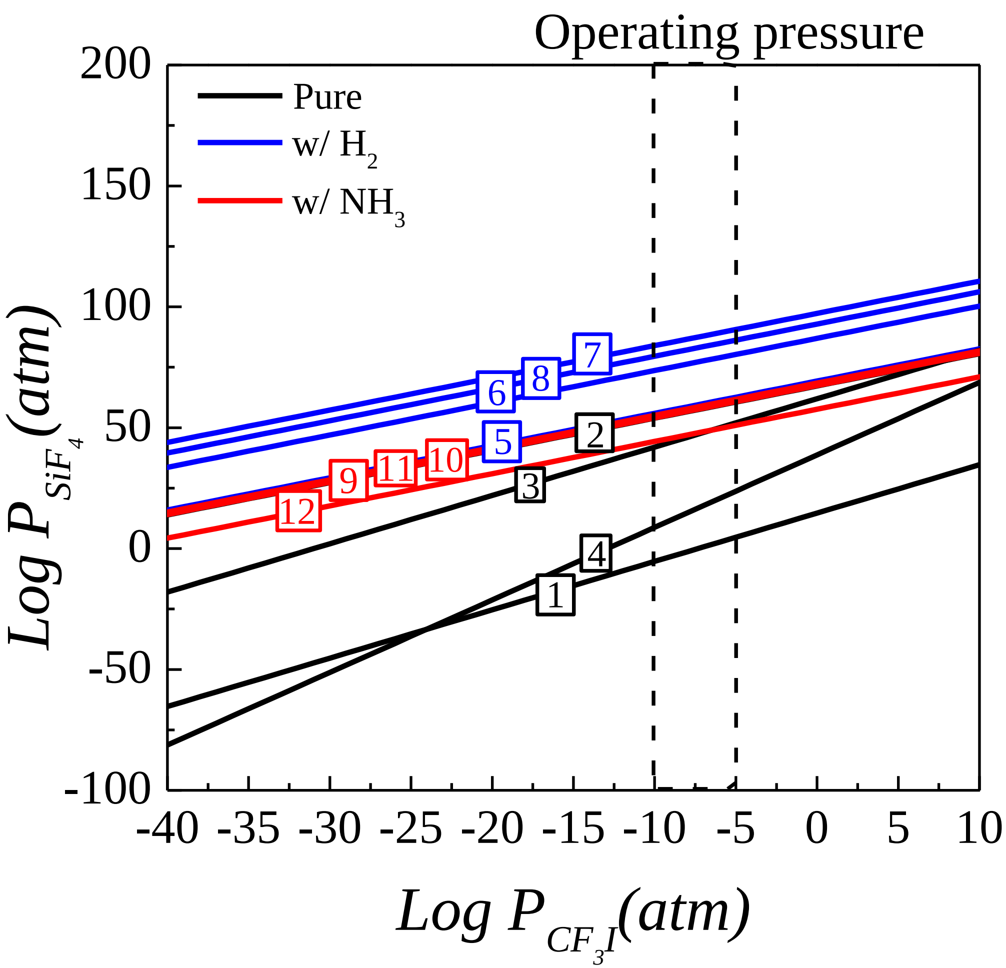
Amount of fluorocarbons detected in exhaust in sccm. Feed gases are all 40 sccm except CF_4 (15 sccm) – CHF_3 (25 sccm).[9]

Etchant	CF_4 (6300)	CHF_3 (12100)	CF_3I (1)	C_2F_6 (12500)	C_3F_8 (6950)	C_2F_4
CF_4	29	0.6	-	2.3	0.6	0.6
CHF_3	4.5	23	-	0.9	0.2	1.6
CF_3I	1.2	-	26	3.4	0.3	1.9
CF_4-CHF_3	11	15	-	1.1	2.9	1.8

- Recombination in plasma forms high-GWP gases (CF_4, C_2F_6)
  - CF_3I has less than 1/3 total impact on global warming compared to other fluorocarbons
- CF_3I photolyzes within days in atmosphere to eventually form CO_2, HF, and HI. [10]
  - This is responsible for GWP_{100} values ≈1.
  - When released from sea level, CF_3I has small effect on ozone (ozone depletion potential = 0.018). [11]

[9] F. Fracassi, R. d'Agostino, J. Vac. Sci. Tech. B 16, 1867 (1998).

Etching with CF_3I

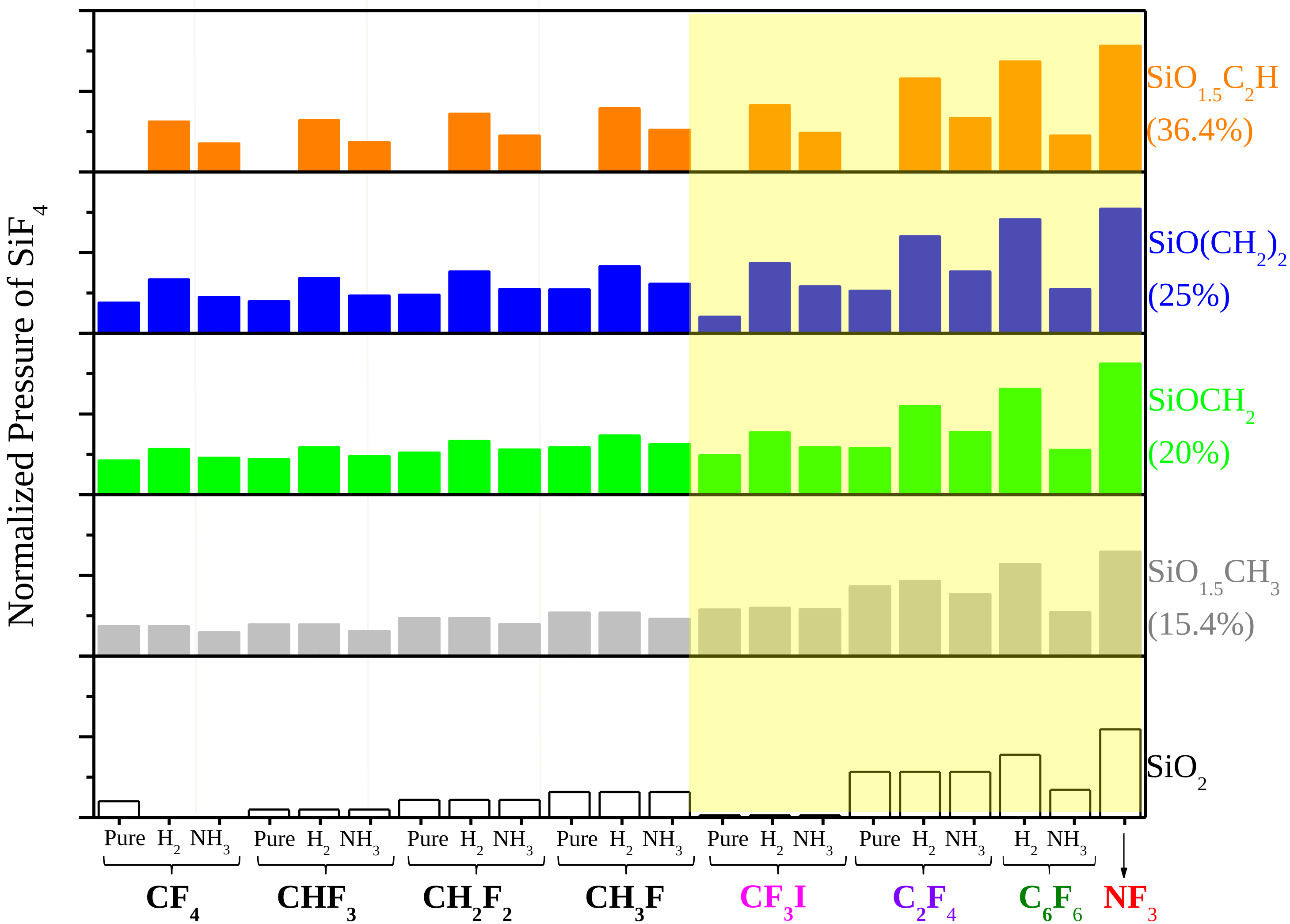


	Reaction	G (eV) [4,5,6]
[1]	$\mathbf{SiO_2}$(c) + 2CF_3I(g) → SiF_4(g) + 2CO(g) + 2IF(g)	-0.87
[2]	6$\mathbf{SiO_{1.5}CH_3}$(c) + 8CF_3I(g) → 6SiF_4(g) + 4I_2(g) + 9CO(g) + C_2H_6(g) + 3CH_4(g)	-24.02
[3]	$\mathbf{SiOCH_2}$(c) + 2CF_3I(g) → SiF4(g) + $C_2H_2F_2$(g) + CO(g) + I_2(g)	-3.69
[4]	$\mathbf{SiO(CH_2)_2}$(c) + 3CF_3I(g) → SiF_4(g) + 2$C_2H_2F_2$(g) + CO(g) + IF(g) + I_2(g)	-2.31
[5]	6$\mathbf{SiO_{1.5}CH_3}$(c) + 8CF_3I(g) + $\mathbf{H_2}$(g) → 6SiF_4(g) + 4I_2(g) + 9CO(g) + 5CH_4(g)	-24.75
[6]	3$\mathbf{SiOCH_2}$(c) + 4CF_3I(g) + 5$\mathbf{H_2}$(g) → 3SiF_4(g) + 3CO(g) + 4CH_4(g) + 2I_2(g)	-15.53
[7]	3$\mathbf{SiO(CH_2)_2}$(c) + 4CF_3I(g) + 8$\mathbf{H_2}$(g) → 3SiF_4(g) + 2I_2(g) + 3CO(g) + 7CH_4(g)	-17.37
[8]	6$\mathbf{SiO_{1.5}C_2H}$(c) + 8CF_3I(g) + 19$\mathbf{H_2}$(g) → 6SiF_4(g) + 4I_2(g) + 9CO(g) + 11CH_4(g)	-33.17
[9]	18$\mathbf{SiO_{1.5}CH_3}$(c) + 24CF_3I(g) + $\mathbf{NH_3}$(g) → 18SiF_4(g) + 12I_2(g) + HCN(g) + 27CO(g) + 14CH_4(g)	-72.25
[10]	9$\mathbf{SiOCH_2}$(c) + 12CF_3I(g) + 5$\mathbf{NH_3}$(g) → 9SiF_4(g) + 9CO(g) + 5HCN(g) + 7CH_4(g) + 6I_2(g)	-36.66
[11]	9$\mathbf{SiO(CH_2)_2}$(c) + 12CF_3I(g) + 8$\mathbf{NH_3}$(g) → 9SiF_4(g) + 6I_2(g) + 9CO(g) + 8HCN(g) + 13CH_4(g)	-36.23
[12]	18$\mathbf{SiO_{1.5}C_2H}$(c) + 24CF_3I(g) + 19$\mathbf{NH_3}$(g) → 18SiF_4(g) + 12I_2(g) + 27CO(g) + 19HCN(g) + 14CH_4(g)	-61.77

- H_2 addition increases the etch product pressure – most effective with 25% C-doped silica
- CF_3I w/ and w/o NH_3 – most effective with 20% C-doped silica

[4] NIST-JANAF Thermochemical (2013)

Comparison of Etch Chemistries



The y-axis represents the normalized partial pressure of SiF_4, one of the primary etch products. The normalization is with respect to the partial pressure of SiF_4 generated in CF_4 etching SiO_2 where all the thermodynamic data are from NIST JANAF Thermodynamic Table, 2013

SRC Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

[4] NIST-JANAF Thermochemical (2013)

Summary

- Volatility diagrams can be used to assess general trends in potential etchant chemistries
- Thermodynamic properties of carbon doped silicon model compounds were evaluated via established bond and group additivity methods
- Addition of hydrogen via H_2 in general increases the pressure of the primary etch product
- Non-PFC alternative chemistries C_2F_4, C_6F_6, NF_3, and CF_3I are shown to be more effective in producing SiF_4 from each of the carbon doped species than fluoromethanes (e.g. CF_4, CHF_3, etc)
- With the exception of NF_3, each of the etchants examined have relatively low global warming potentials (GWPs); however, NF_3 can be effectively abated through thermal processes
- CF_3I is not as effective as NF_3, yet still viable, due to less environmental impact

Reference

[1] Vasarla Nagendra Sekhar (2012). Mechanical Characterization of Black Diamond (Low-k) Structures for 3D Integrated Circuit and Packaging Applications, Nanoindentation in Materials Science, Dr. Jiri Nemecek (Ed.), ISBN: 978-953-51-0802-3, InTech, DOI: 10.5772/53198. Available from: http://www.intechopen.com/books/nanoindentation-in-materials-science/mechanical-characterization-of-black-diamond-low-k-structures-for-3d-integrated-circuit-and-packaging

[2] W. Volksen, R. D. Miller, G. Dubois, *Chem. Rev.* **110**, 56 (2010).

[3] S. W. Benson and Norman Cohen, "Chapter 2, Current Status of Group Additivity" compiled by Karl K. Irikura and David J. Frurip, in "Computational Thermochemistry," ACS Symposium series 677, (1988).

[4] NIST-JANAF Thermochemical Tables. http:// http://kinetics.nist.gov/janaf/ (accessed 2013).

[5] H. E. O'Neal, M. A. Ring, *Inorganic Chemistry* 5, 435 (1966).

[6] CRC Handbook of Chemistry and Physics. http:// www.hbcpnetbase.com/ (accessed August 12, 2013).

[7] K. Yonekura, et al., *J. Vac. Sci. Tech. B* **22**, 548 (2004).

[8] E. Soda, et al. *J. Vac. Sci. Tech. A* **26**, 875 (2008).

[9] F. Fracassi, R. d'Agostino, *J. Vac. Sci. Tech. B* **16**, 1867 (1998).

[10] Committee on Assessment of Fire Suppression Substitutes and Alternatives to Halon, Naval Studies Board, Commission on Physical Sciences, Mathematics, and Applications, National Research Council, *Fire Suppression Substitutes and Alternatives to Halon for U.S. Navy Applications*; National Academy Press: Washington, D.C., 1997.

[11] Y. Li, K. O. Patten, D. Youn, D. J. Wuebbles, *Atmos. Chem. Phys.* **6**, 4559 (2006).

[12] United Nations Environment Program(UNEP), 2010.

[13] W. Tsai, J. Hazard. Mater., 2008.

[14] Ammonia as a Refrigerant, ASHRAE, 2006.

[15] S.Takahashi, et al. Japan. J. Appl. Phys. **44,** L781 (2005).

[16] R. Chatterjee, et al. J. Elec. Soc. **148**, 12 (2001).

[17] PFC reduction/Climate partnership for the semiconductor industry, US EPA (U.S. Environmental Protection Agency), (2008) (http://www.epa.gov/semiconductor-pfc/basic.html)

[18] W. Worth, PFC Technical Update Session, SEMICON/WEST(1995)