Non-PFC Plasma Chemistries for Patterning Complex Materials/Structures

(Task Number: 425.038)

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Other Researchers:

- **(TBD)**

Objectives

- **Assess the thermodynamic feasibility of patterning etch-resistant materials (complex materials and structures)**
- **Identify the non-PFC alternative for through silicon via etch**
- **Validate the theoretical assessment by performing etching experiments of these materials by industrial sponsors**

	Features	Goal	Ref.
1	Etch rate	50 um/min	I. Sakai, J. Vac. Sci. Technol. A, 2011
2	Aspect ratio (Anisotropy)	70-100	I. Sakai, IEEE, 2012
3	Side wall angle	$90^{o} \pm 10^{o}$	M. Hooda, J. Vac. Sci. Technol. A, 2010

ESH Metrics and Impact

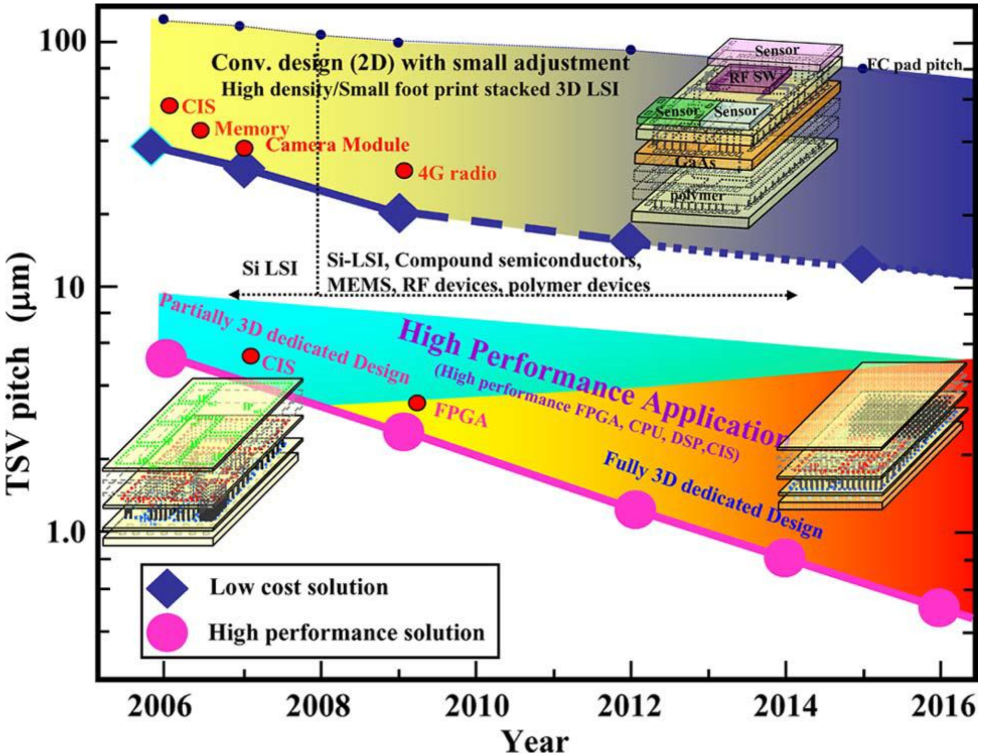
1. **Reduction in the use of PFC gases by focusing on non-PFC chemistries**

2. **Reduction in emission of PFC gases to environment**

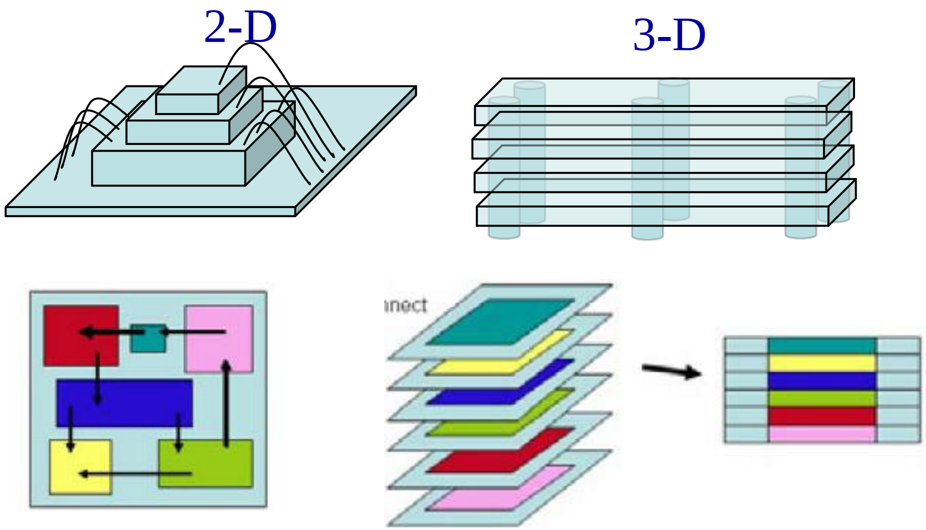
3. **Reduction in the use of chemicals by tailoring the chemistries to the specific materials to be removed**

TSV (Through Silicon Via)

TSV for 3D-LSI technology road map [1]



From 2-D to 3-D packaging [2]



Advantages:

- Smaller footprint and form-factor
- Less weight and power consumption
- Potentially lower cost

- According to Moore's Law, the density of IC devices doubles every two years, the 3-D packaging system is required.

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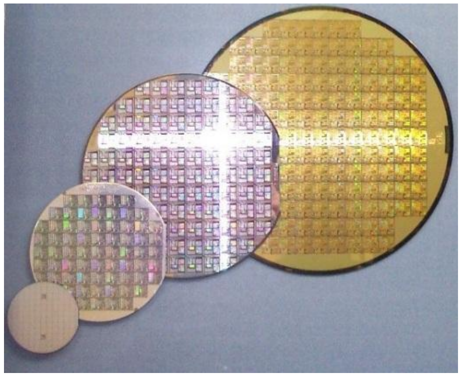
[1] M. Motoyoshi, IEEE, 2009; [2] P. Garrou, Samsung website, 2010

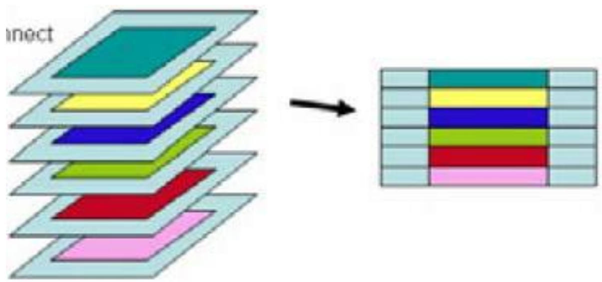
Challenges in TSV

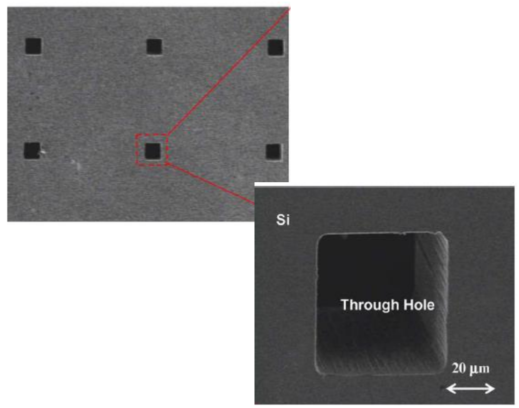
High etch rate (~1 μm/min)



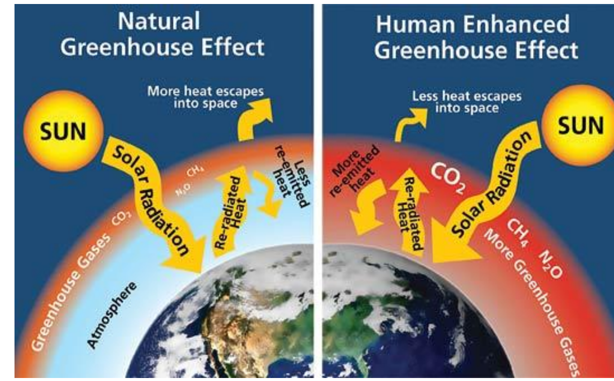
Silicon size (inch)	Thickness (um)
6	**675**
8	**725**
12	**775**
18	**925**

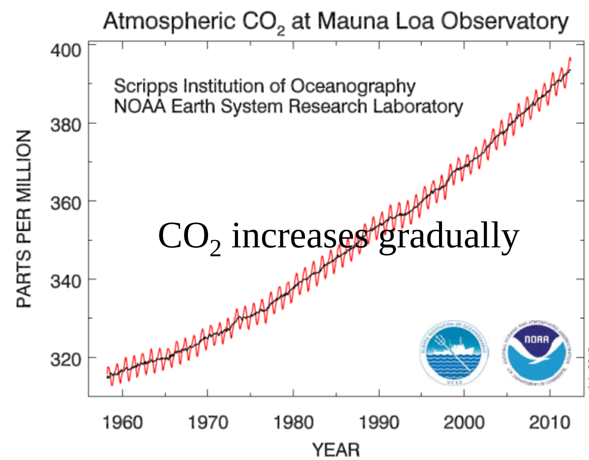
High aspect ratio (>10) [1, 2]





Greenhouse gas usage [3]





- Requirement to increase etch rate, increase aspect ratio and reduce the usage of global warming gases

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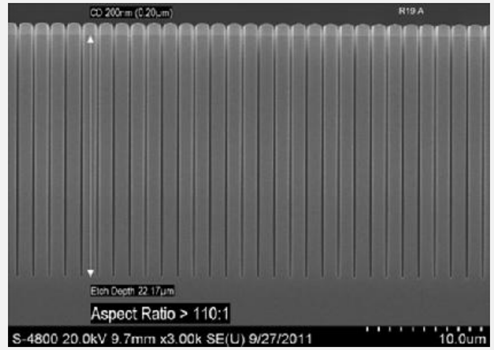
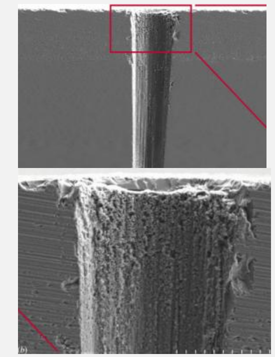
[1] M. Motoyoshi, IEEE, 2009; [2] P. Garrou, Samsung website, 2010; [3] NOAA Earth System Research Laboratory, 2012

TSV Process Options





TSV Processes	DRIE (Deep Reactive Ion Etching) [4]		Laser drill [5]
	Bosch DRIE [6]	Cryogenic DRIE [7]	Laser drill [5]
Width	<5μm	<5μm	<15μm
Aspect ratio	>20:1	>10:1	>7:1
Sidewalls	Vertical (90^o)	Vertical &smooth	80^o-90^o
Temp. affection	Negligible	-110^{o}C ~ -130^{o}C	Yes
Process	ICP	ICP	Laser
Potential applications	High-end	High-end	Low-cost
Example	Microprocessors	Microprocessors	DRAM/Flash

- As the critical dimension continues to decrease, DRIE becomes the most feasible technology for TSV

[4] Applied Materials Inc., website, 2012; [5]C. Tang, J Micromech Microeng,2012; [6] R. Landgraf, IEEE, 2008; [7] M. Walker, Proc. SPIE, 2001

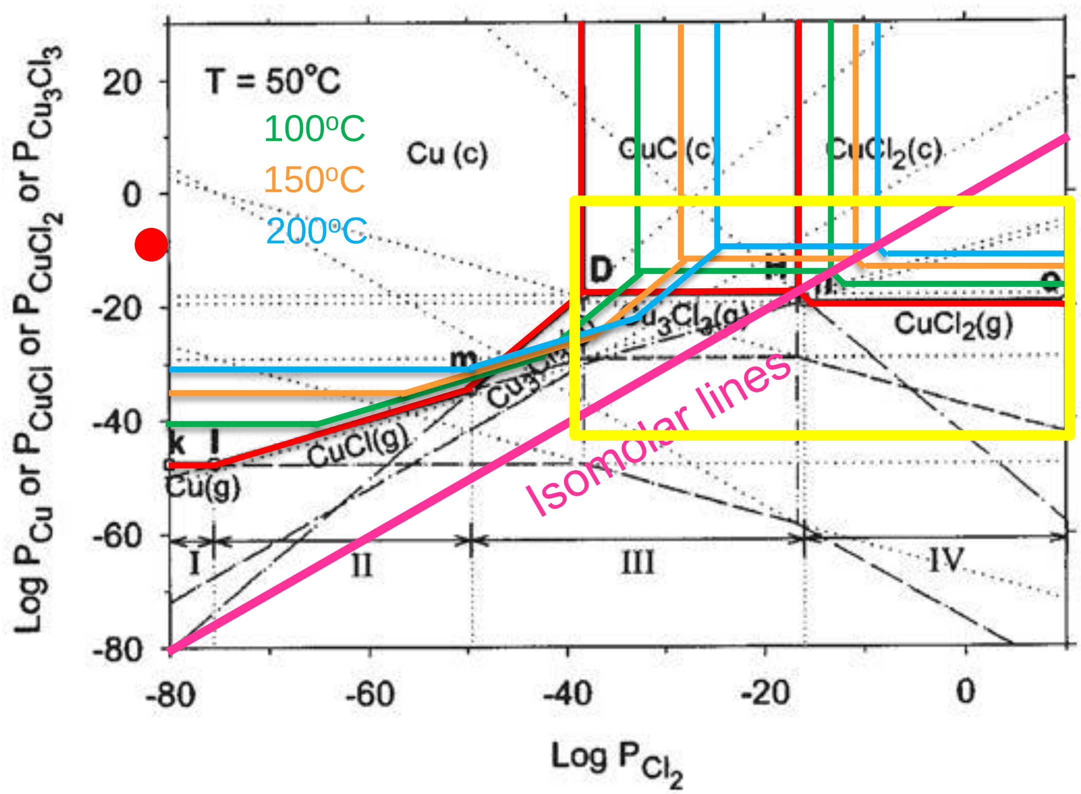
Systematic Approach - Thermodynamics

- **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**

A Case Study Cu-Cl of Volatility Diagram [8]

No.	Reaction
1	$Cu(c) + 1/2Cl_2(g) = CuCl(c)$
2	$CuCl(c) + 1/2Cl_2(g) = CuCl_2(c)$
3	$Cu(c) = Cu(g)$
4	$CuCl(c) = Cu(g) + 1/2Cl_2(g)$
5	$CuCl_2(c) = Cu(g) + Cl_2(g)$
6	$Cu(c) + 1/2Cl_2(g) = CuCl(g)$
7	$CuCl(c) = CuCl(g)$
8	$CuCl_2(c) = CuCl(g) + 1/2Cl_2(g)$
9	$Cu(c) + Cl_2(g) = CuCl_2(g)$
10	$CuCl(c) + 1/2Cl_2(g) = CuCl_2(g)$
11	$CuCl_2(c) = CuCl_2(g)$
12	$3Cu(c) + 3/2Cl_2(g) = Cu_3Cl_3(g)$
13	$3CuCl(c) = Cu_3Cl_3(g)$
14	$3CuCl_2(c) = Cu_3Cl_3(g) + 3/2Cl_2(g)$

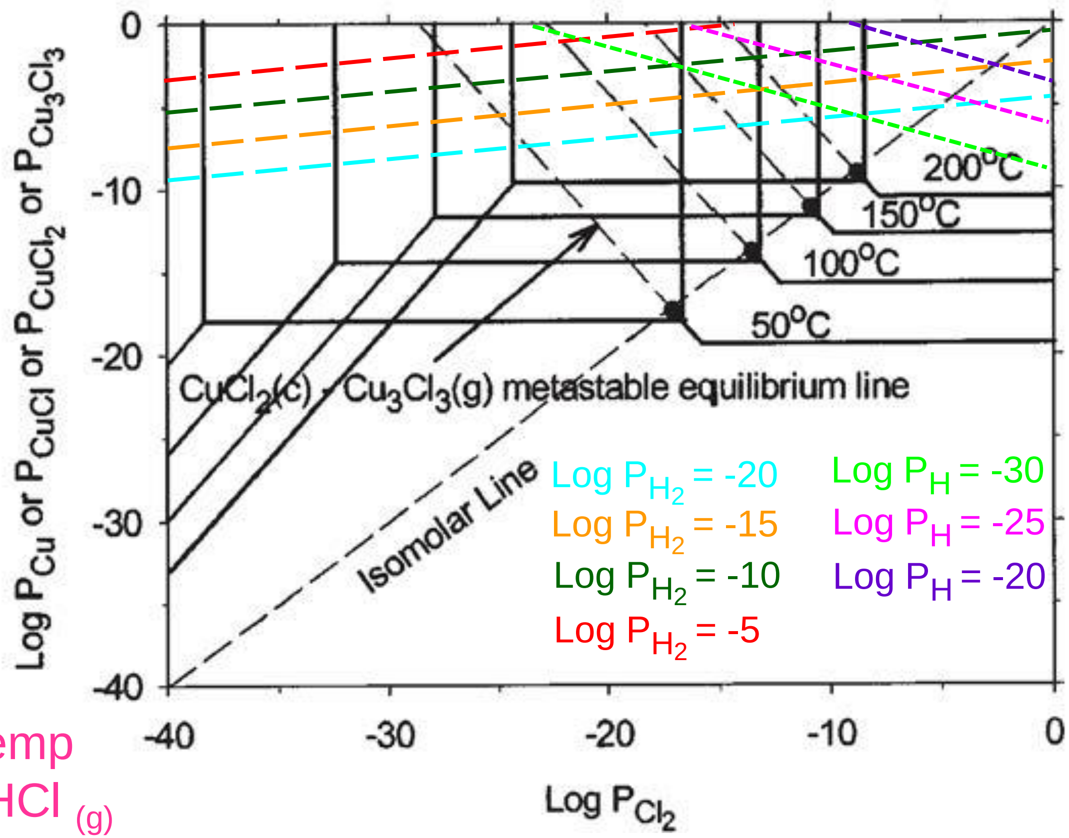


- Target the volatile species
- Control pressure, temperature and gas composition

[8] N.S. Kulkarni, J. Electrochem. Soc., 2002

A Case Study Cu-Cl-H of Volatility Diagram [8]

No.	Reaction
1	$Cu(c) + 1/2H_2(g) = CuH(g)$
2	$Cu(c) + H(g) = CuH(g)$
3	$CuCl(c) + 1/2H_2(g) = CuH(g) + 1/2Cl_2(g)$
4	$CuCl(c) + H(g) = CuH(g) + 1/2Cl_2(g)$
5	$CuCl_2(c) + 1/2H_2(g) = CuH(g) + Cl_2(g)$
6	$CuCl_2(c) + H(g) = CuH(g) + Cl_2(g)$
7	$3CuCl_2(c) + 3/2H_2(g) = Cu_3Cl_3(g) + 3HCl(g$
8	$3CuCl_2(c) + 3H(g) = Cu_3Cl_3(g) + 3HCl(g)$
9	$CuCl_2(c) + 3/2H_2(g) = CuH(g) + 2HCl(g)$
10	$CuCl_2(c) + 3H(g) = CuH(g) + 2HCl(g)$
11	$CuCl(c) + H_2(g) = CuH(g) + HCl(g)$
12	$CuCl(c) + 2H(g) = CuH(g) + HCl(g)$



Proposed two-step reaction (2002):

1) $Cu_{(c)} + 2Cl_{(g)} \rightarrow CuCl_{2(c)}$ at low temp

2) $3 CuCl_{2(c)} + 3H_{(g)} \rightarrow Cu_3Cl_{3(g)} + 3HCl_{(g)}$

→ Experimentally verified by Hess in 2007/2011

- Addition of reactive chemistry (H_2/H) changed the reaction kinetics and resulted in higher etch rates

[8] N.S. Kulkarni, J. Electrochem. Soc., 2002

Important Chemistries for Silicon Etch [9]

Chemistries	Radical	Volatile Product	Inhibitor
H_2	H	$HSiF_4$	Si_xF_y
CH_4	CH_3 CH_2	SiH_4 SiF_4	$Si_xC_yH_z$
F_2	F	SiF_4	Si_xF_y
NF_3	F, NF_2	SiF_4	$Si_xN_yF_z$
SiF_4	F, SiF_3	SiF_4	Si_xF_y
CF_4	F, CF_3	SiF_4	$Si_xC_yF_z$
SF_6	F, SF_5	SiF_4	$Si_xS_yF_z$
S_2F_2	F, S_2F	SiF_4	$Si_xS_yF_z$
Cl_2	Cl	$SiCl_4$	Cl
Br_2	Br	$SiBr_4$	Br
CBr_4	Br, CBr_3	$SiBr_4$	$Si_xC_yBr_z$, Br

Chemistries	Radical	Volatile Product	Inhibitor
CHF_3	CF_2	HF, SiF_4	$Si_xC_yH_z$
CH_2F_2	CFH, C	HF	$Si_xC_yF_zH_a$
CH_3F	CH2 CFH	HF, H_2	$Si_xC_yF_zH_a$
CF_4/O_2	F, O, CF_3	COF_2, O_2F, OF, F_2, SiF_4	$Si_xO_yF_z$
CF_4/H_2	F, H, CF_3	CHF, HF, SiF_4	$Si_xC_yF_z$
SF_6/O_2	SF_5, O, F	SOF_4, SiF_4	$Si_xO_yF_z$
SF_6/H_2	SF_5, H, F	HF, SiF_4	$Si_xS_yF_z$
SF_6/N_2	SF_5, N_2, F	SiF_4	$Si_xS_yF_z$
SF_6/CHF_3	SF_5, F, CF_2	HF, SiF_4	$Si_xC_yF_z$
$CBrF_3$	F, Br	$SiBr_4$	Br, $Si_xC_yF_z$ $Si_xC_yBr_z$
CCl_4	CCl_3, Cl, C	$SiCl_4$	Cl

→*Fluorine-based gases remains the most effective chemistry*

[9]H. Jansen, J. Mrcromech. Microeng. 1996

Can SF_6 be replaced for Si etching

Chemistries	Atmospheric conc. in 2005 (ppt)	Con. since 1994* & 1998 (ppt)	Annual emission in late 1990s (Gg)	Rafactive efficiency (W/m^2 –ppbv)	Lifetime (year)	Global warming potential	Ref.
CO_2	$278x10^6$	$358x10^6$*	-	-	variable	1	[10]
CH_4	$7x10^5$	$1721x10^3$*	-	-	12.2	21	[10]
N_2O	$275x10^3$	$311x10^3$*	-	-	120	310	[10]
$CHClF_2$	-	$105x10^3$*	-	-	12.1	1400	[10]
CF_4	74	-	~15	0.1	50,000	6500	[11]
CCl_2F_2	-	$503x10^3$*	-	-	102	7100	[10]
C_2F_6	2.9	3.4	~2	0.26	10,000	9200	[11]
CHF_3	18	22	~7	0.19	270	11700	[11]
SF_6	5.6	7.1	~6	0.52	3,200	23900	[11]
NF_3	<0.1	-	~2.3	0.21	740	16800	[11]

→ GWPs are one type of simplified index based upon radiative properties which estimate the potential future impacts of gases

→ NF_3 is promising but it is a Greenhouse gas.

[10] United Nations Environment Program(UNEP), 2010; [11] W. Tsai, J Hazard Mater, 2008

The potential use of NF_3 in TSV

- NF_3 and its reaction products are toxic in Toxic Substances Control Act (TSCA)
- $NF_3 + 2H_2O \rightarrow 3HF + HNO_2$; $NF_3 + 3H_2O \rightarrow 6HF + NO + NO_2$; $2NF_3 + 3H_2 \rightarrow N_2 + 6HF$

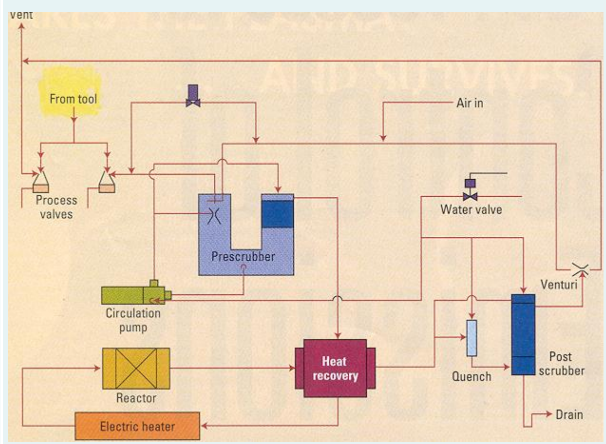
Title	Authors	Year	Journal	Citation
NF_3,the greenhouse gas missing from Kyoto	Prather, M.J. and J. Hsu	2010	Geophysical Research Letters	55444
Environmental and health risk analysis of NF_3, a toxic and potent greenhouse gas	Tsai, W. T.	2008	Journal of Hazardous Materials	28060

- Abatement of Greenhouse Gases [12]:

BOE Edwards Thermal Processing System

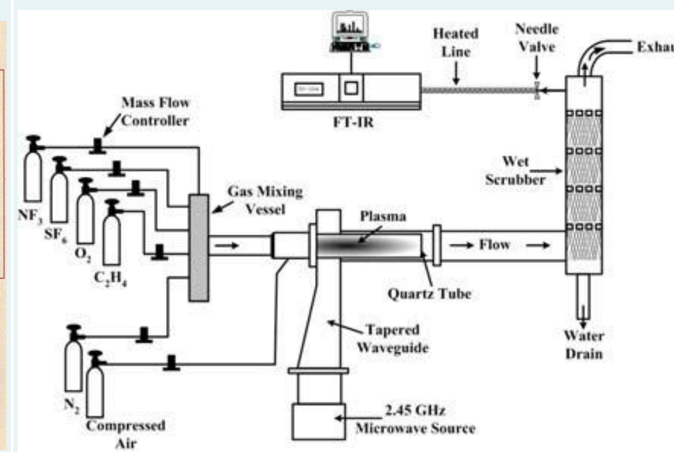
Not effective in decomposing CF_4

Catalytic Decomposition Systems



The catalyst lifetime only 18 months

Plasma Abatement Systems

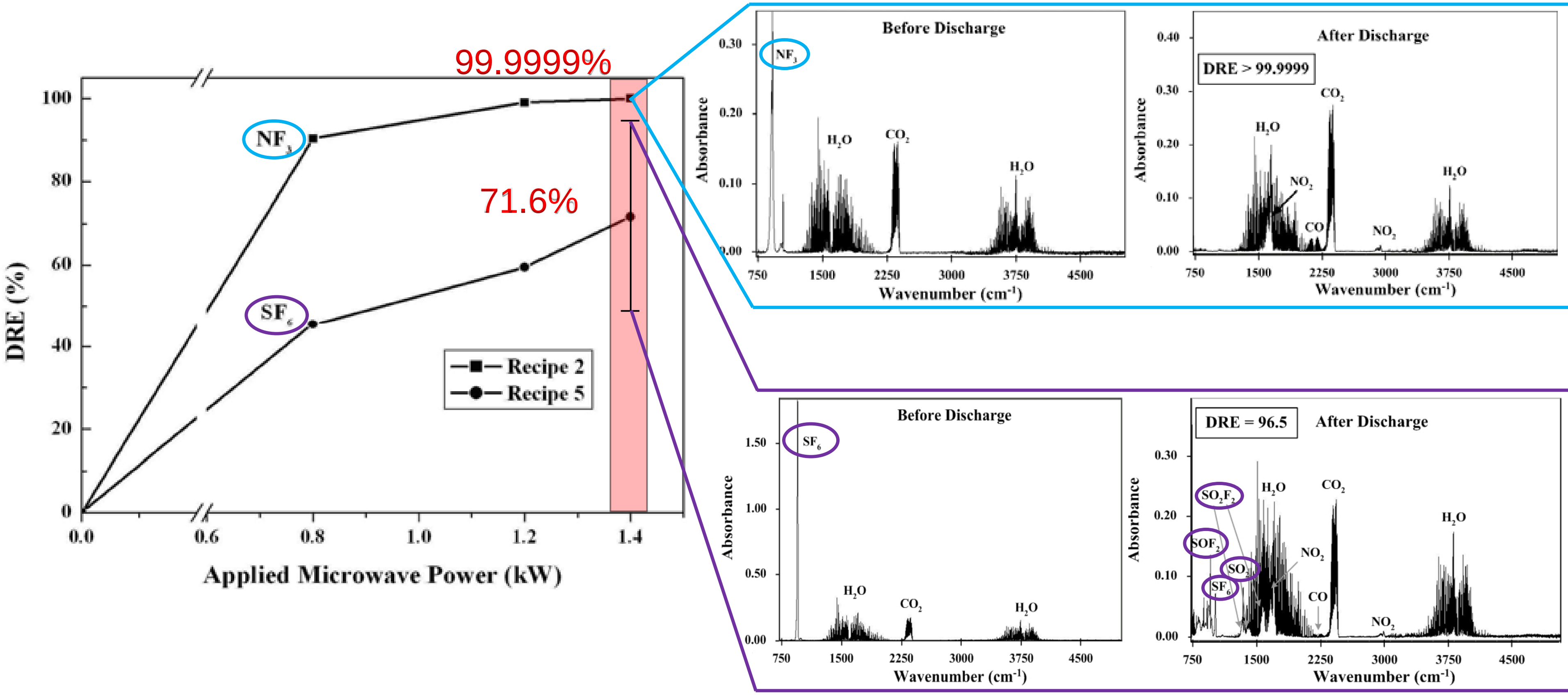


For semiconductor industry in plasma etching process and chamber cleaning

[12] Vasilis Fthenakis, U.S. DOE, 2001

Plasma Torch Abatement of NF_3 & SF_6[13]

- Destruction and removal efficiency (DRE) = $\frac{C_{before} - C_{after}}{C_{before}} \times 100$



→ NF_3 is a Greenhouse gas but it can be destroyed nearly 100%

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[13] Yong C. Hong, IEEE, 2005

Etch Rate of Si /poly-Si* in F-based chemistries

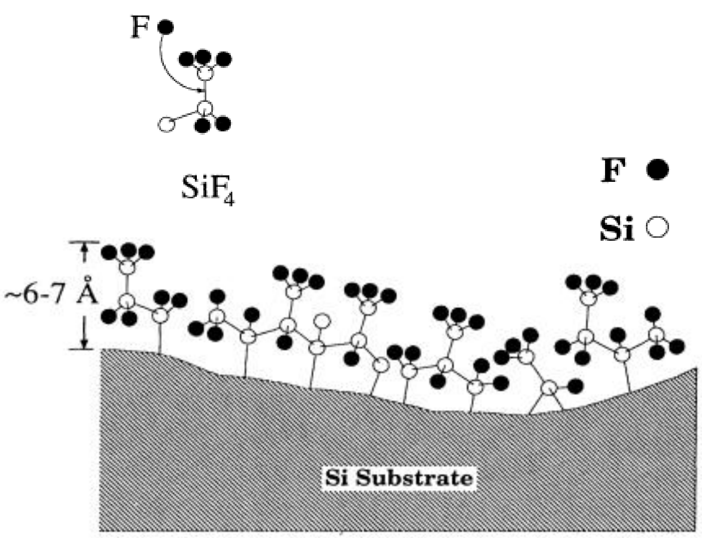
Etchant	Etch rate (nm/min)	Power (W)	Pressure (mtorr)	Ref
SF_6	300		20	[g]
SF_6/O_2(25%)	880	300	25	[d]
SF_6/O_2(25%)	490		100	[d]
$SF_6/O_2/CHF_3$	3000	500		[c]
SF_6(40sccm)/O_2(14sccm)/CHF_3(17sccm)	670		60	[j]
SF_6(80%)/$C_2Cl_3F_3$(20%)	700	140	47	[i]
SF_6(10%)/$CBrF_3$(90%)	310	100	50	[h]
SF_6(6sccm)/HBr(10sccm)/Cl_2(70sccm) *	1100		100	[e]
SF_6(10%)/$CBrF_3$(80%)/Ar(10%)	410	190	50	[h]
CF_4	30			[k]
CF_4 *	20			[f]
CF_4/O_2	460			[k]
CF_4/O_2	300			[k]
CF_4(90%)/O_2(12%)/N_2(8%) *	260			[e]
$CBrF_3$	60	100	50	[h]
$CBrF_3$	40	100	20	[g]
F/F_2	460			[k]
SiF_4/O_2	44			[k]

Etch Rate of $Si/SiO_2/Si_3N_4/SiC$ by NF_3

Etchant	Etch rate_Si (nm/min)	Etch rate_SiO_2 (nm/min)	Etch rate_Si_3N_4 (nm/min)	Etch rate_SiC (nm/min)	Power	Pressure (mtorr)	Ref
NF_3(100%)		90	1000		1.4W/cm^2	550	[l]
NF_3(25%)/N_2		860	7400		1.4W/cm^2	550	[l]
NF_3(25%)/Ar		670	8000		1.4W/cm^2	550	[l]
NF_3(25%)/He		560	7400		1.4W/cm^2	550	[l]
NF_3(25%)/O_2		520	5200		1.4W/cm^2	550	[l]
NF_3(25%)/N_2O		280	3600		1.4W/cm^2	550	[l]
NF_3				437	900W	12	[m]
NF_3/O_2				350	750W	2	[n]
NF_3(60%)/CH_4(40%)				111	800W	6	[m]
NF_3(7sccm)	192				40W	100	[o]
NF_3(300sccm)	550	30	18		1400W	1000	[p]
NF_3(500sccm)/O_2(50%)		90	360		1400W	1000	[p]
NF_3(200sccm)	380				1400W	1	[q]
NF_3(10%)/O_2(90%)	700				1400W	1	[q]

- The addition of O_2 seems to increase Si, SiO_2 and Si_3N_4 etch rate

Silicon Etching by Fluorine



Main reactions of silicon etching by F_2

	Reactions	G(eV)	log(K)
1	$Si(c) \rightarrow Si(g)$	4.20	-70.5
1’	$Si(c) + \frac{1}{2}F_2(g) \rightarrow SiF(g)$	-0.54	9.0
2	$Si(c) + F(g) \rightarrow SiF(g)$	-1.18	19.8
3	$SiF(g) + F(g) \rightarrow SiF_2(g)$	-6.31	105.9
4	$SiF_2(g) + F(g) \rightarrow SiF_3(g)$	-5.57	93.4
5	$SiF_3(g) + F(g) \rightarrow SiF_4(g)$	-5.82	97.7

Electron impact dissociate energy of F_2[14]

Reactions	G(eV)
$F_2(g) + e \rightarrow 2F(g) + e$	1.6

- Fluorine is the most effective etching chemistry for silicon, especially atomic fluorine, as produced by plasma

[14] Parker J., J. Quant. Electron., 1973

Production of Fluorine from SF_6 and NF_3

	Thermal Dissociate Rxns	G(eV)	Log(K)
S1	$SF_6(g) \rightarrow SF_5(g) + F(g)$	3.52	-59.1
S2	$SF_5(g) \rightarrow SF_4(g) + F(g)$	1.85	-31.0
S3	$SF_4(g) \rightarrow SF_3(g) + F(g)$	3.07	-51.5
S4	$SF_3(g) \rightarrow SF_2(g) + F(g)$	2.56	-42.9
S5	$SF_2(g) \rightarrow SF(g) + F(g)$	3.64	-61.1
S6	$SF(g) \rightarrow S(g) + F(g)$	3.25	-54.6

	Thermal Dissociate Rxns	G(eV)	Log(K)
N1	$NF_3(g) \rightarrow NF_2(g) + F(g)$	2.17	-36.4
N2	$NF_2(g) \rightarrow NF(g) + F(g)$	2.58	-43.3
N3	$NF(g) \rightarrow N(g) + F(g)$	2.84	-47.7

[CRC handbook, 2010]

[CRC handbook, 2010*; Y. Tanaka, IEEE, 1997]

	Electron Impact Dissociate Rxns	G(eV)
S1	$SF_6(g) + e \rightarrow SF_5(g) + F(g) + e$	4.00
S2	$SF_5(g) + e \rightarrow SF_4(g) + F(g) + e$	2.27
S3	$SF_4(g) + e \rightarrow SF_3(g) + F(g) + e$	3.47
S4	$SF_3(g) + e \rightarrow SF_2(g) + F(g) + e$	2.92
S5	$SF_2(g) + e \rightarrow SF(g) + F(g) + e$	4.01
S6	$SF(g) + e \rightarrow S(g) + F(g) + e$	3.52

- For SF_6, electron impact dissociate energy is comparable and slightly higher than that of equilibrium data (~0.4eV)

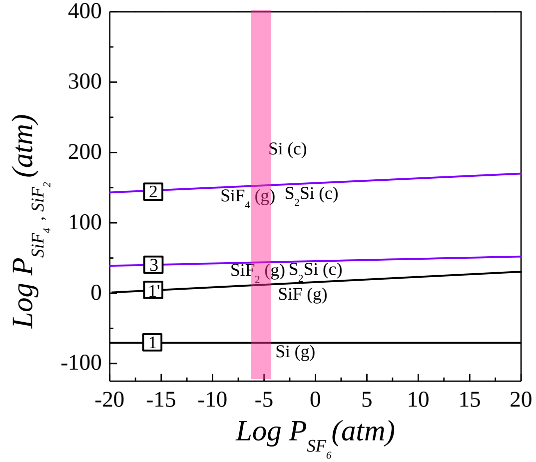
- It is possible that the available equilibrium data on NF_3 can be used as a guide to the production of fluorine in a plasma

Can SF_6 be Replaced by NF_3?

$Si + \frac{1}{2} SF_6(g) \rightarrow \frac{3}{4} SiF_4(g) + \frac{1}{4} SiS_2(c)$

$\Delta G = -7.0eV$

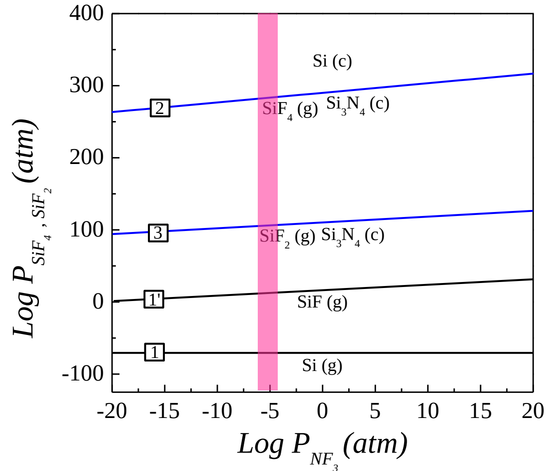
	Reactions	G(eV)	log(K)
1	$Si(c) \rightarrow Si(g)$	4.20	-70.5
1’	$Si(c) + \frac{1}{2}F_2(g) + \rightarrow SiF(g)$	-0.54	9.0
2	$Si(c) + \frac{1}{2}SF_6(g) \rightarrow \frac{1}{4}S_2Si(c) + \frac{3}{4}SiF_4(g)$	-7.00	117.5
3	$Si(c) + \frac{2}{7}SF_6(g) \rightarrow \frac{1}{7}S_2Si(c) + \frac{6}{7}SiF_2(g)$	-2.32	39.0



$Si + \frac{2}{3} NF_3(g) \rightarrow \frac{1}{2} SiF_4(g) + \frac{1}{6} Si_3N_4(c)$

$\Delta G = -8.6eV$

	Reactions	G(eV)	log(K)
1	$Si(c) \rightarrow Si(g)$	4.20	-70.5
1’	$Si(c) + \frac{1}{2}F_2(g) \rightarrow SiF(g)$	-0.54	9.0
2	$Si(c) + \frac{2}{3}NF_3(g) \rightarrow \frac{1}{6}N_4Si_3(c) + \frac{1}{2}SiF_4(g)$	-8.63	145.0
3	$Si(c) + \frac{4}{9}NF_3(g) \rightarrow \frac{1}{9}N_4Si_3(c) + \frac{2}{3}SiF_2(g)$	-4.46	74.9



- NF_3 is more capable of removing silicon via the formation of SiF_4
- However, another significant reaction product from reaction with NF_3 is Si_3N_4, which has to be removed and competes for fluorine

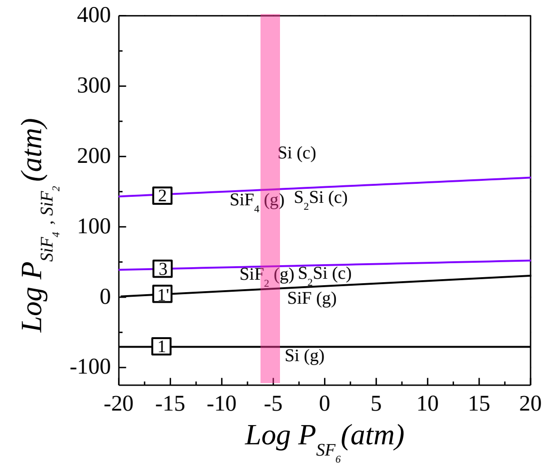
Can SF_6 be Replaced by NF_3?

$$Si + \tfrac{1}{2}\,SF_6(g) \rightarrow \tfrac{3}{4}\,SiF_4(g) + \tfrac{1}{4}\,SiS_2(c) + 4F(g) \rightarrow \tfrac{1}{4}SiF_4(g) + \tfrac{1}{2}SF_6(g)$$

ΔG = -7.0eV

Δ G = - 1.9eV

	Reactions	G(eV)	log(K)
1	$Si(c) \rightarrow Si(g)$	4.20	-70.5
1'	$Si(c) + \tfrac{1}{2}F_2(g) + \rightarrow SiF(g)$	-0.54	9.0
2	$Si(c) + \tfrac{1}{2}SF_6(g) \rightarrow \tfrac{1}{4}S_2Si(c) + \tfrac{3}{4}SiF_4(g)$	-7.00	117.5
3	$Si(c) + \tfrac{2}{7}SF_6(g) \rightarrow \tfrac{1}{7}S_2Si(c) + \tfrac{6}{7}SiF_2(g)$	-2.32	39.0

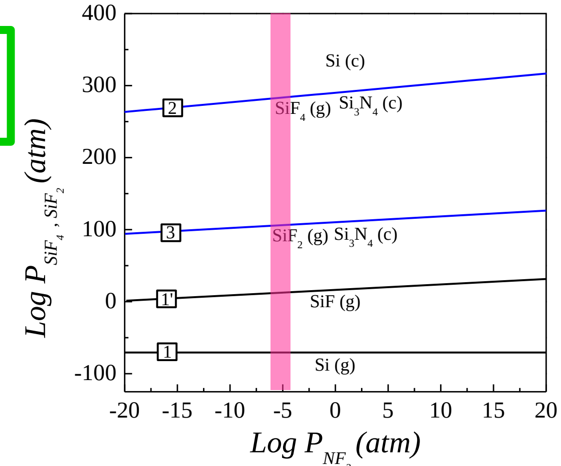


$$Si + \tfrac{2}{3}\,NF_3(g) \rightarrow \tfrac{1}{2}\,SiF_4(g) + \tfrac{1}{6}\,Si_3N_4(c) + 4F(g) \rightarrow \tfrac{1}{2}SiF_4(g) + \tfrac{2}{3}NF_3(g)$$

Δ G = -8.6eV

Δ G = -0.2eV

	Reactions	G(eV)	log(K)
1	$Si(c) \rightarrow Si(g)$	4.20	-70.5
1'	$Si(c) + \tfrac{1}{2}F_2(g) \rightarrow SiF(g)$	-0.54	9.0
2	$Si(c) + \tfrac{2}{3}NF_3(g) \rightarrow \tfrac{1}{6}N_4Si_3(c) + \tfrac{1}{2}SiF_4(g)$	-8.63	145.0
3	$Si(c) + \tfrac{4}{9}NF_3(g) \rightarrow \tfrac{1}{9}N_4Si_3(c) + \tfrac{2}{3}SiF_2(g)$	-4.46	74.9



- NF_3 is more capable of removing silicon via the formation of SiF_4
- However, another significant reaction product from reaction with NF_3 is Si_3N_4, which has to be removed and competes for fluorine

A Strategy to Remove Si_3N_4 by O_2 addition

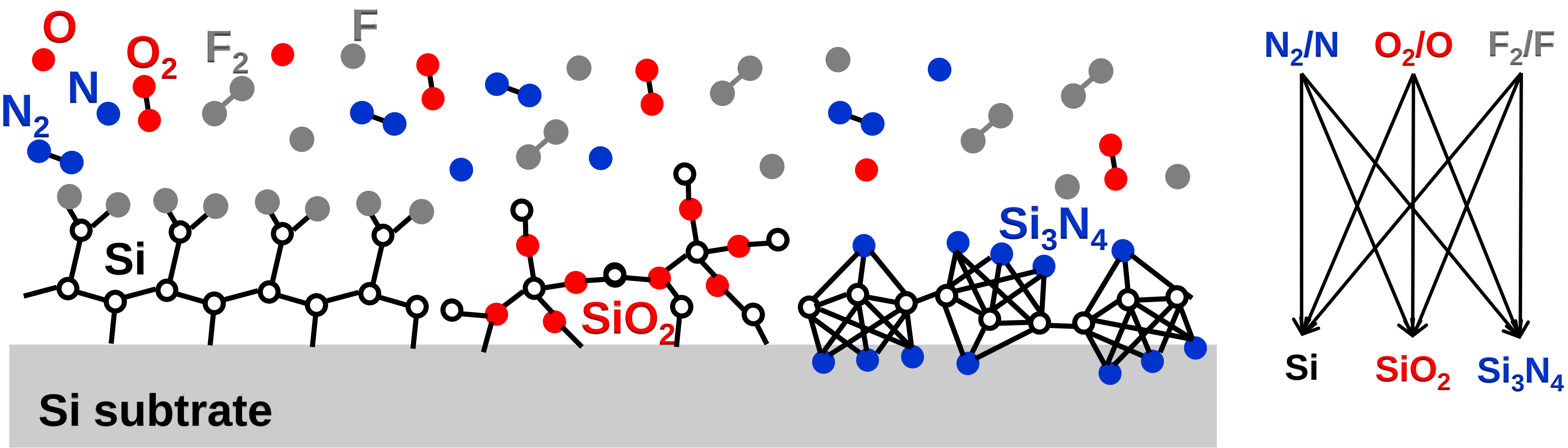
Formation of $Si_3N_4(c)$	ΔG(eV)
$Si(c) + \frac{2}{3}NF_3(g) \rightarrow \frac{1}{2}SiF_4(g) + \frac{1}{6}Si_3N_4(c)$	-8.6

Removal of $Si_3N_4(c)$ by F	ΔG(eV)
$\frac{1}{6}Si_3N_4(c) + 4F(g) \rightarrow \frac{1}{2}SiF_4(g) + \frac{2}{3}NF_3(g)$	-10.2

	Removal of $Si_3N_4(c)$ & $SiO_2(c)$ by NF_3 & O_2	ΔG (eV)
Removal of $Si_3N_4(c)$	$\frac{1}{6}Si_3N_4(c)+\frac{7}{6}O_2(g)\rightarrow\frac{1}{2}SiO_2(c)+\frac{2}{3}NO_2(g)$	-3.0
Removal of $SiO_2(c)$	$\frac{1}{2}SiO_2(c)+\frac{5}{4}NF_3(g)\rightarrow\frac{1}{2}SiF_4(g)+\frac{1}{4}NO_2F(g)+\frac{1}{2}NOF_3(g)+\frac{1}{2}N_2(g)$	-3.3
Total reaction	$\frac{1}{6}Si_3N_4(c)+\frac{7}{6}O_2(g)+\frac{5}{4}NF_3\rightarrow\frac{1}{2}SiF_4(g)+\frac{1}{4}NO_2(g)+\frac{1}{4}NO_2F(g)+\frac{1}{2}NOF_3(g)+\frac{1}{2}N_2(g)$	-6.3

- From the analysis of ΔG, the non-volatile byproducts, Si_3N_4 could be removed by NF_3 - O_2 (as a mixture)

Surface of Silicon (NF_3/O_2)



Gas phase

- The interaction of N/O/F need to be determined

Surface

- Since Si(c), SiO_2(c) and Si_3N_4(c) are non-volatile compounds, they all need to be removed by the plasma

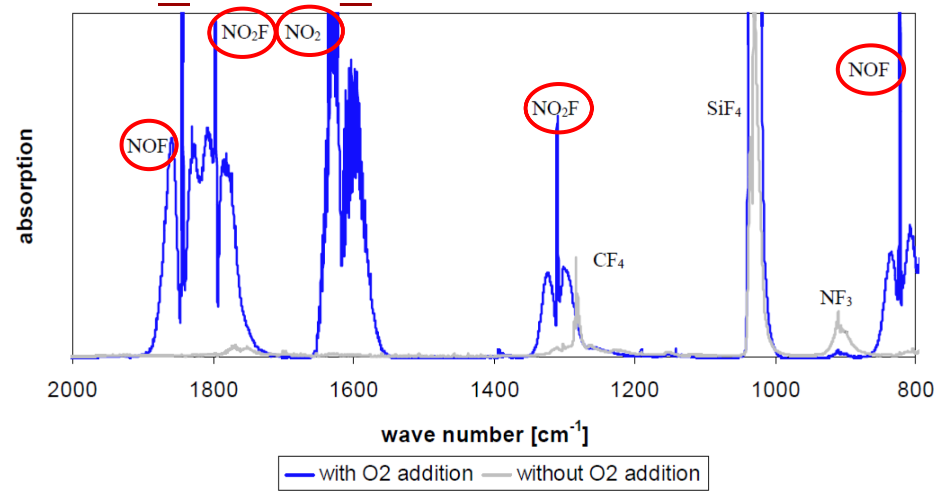
	ΔG(eV) [15]
$NO_2F(g)$	-0.69
NOF(g)	-0.52

Gas phase - O_2/NF_3

- From the FTIR of NF_3/O_2 silicon etching[17], $NO_2F(g)$, NOF(g) and NO(g) can be found when the NF_3 with O_2 addition.
- The following reactions have been proposed,

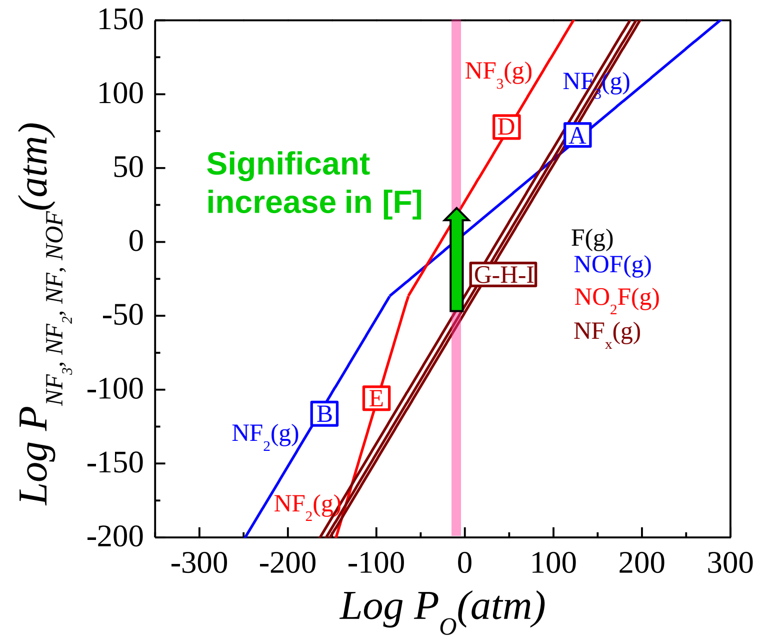
$$O(g) + NF_x(g) \rightarrow NOF(g) + (x\text{-}1)F(g)$$

$$2O(g) + NF_x(g) \rightarrow NO_2F(g) + (x\text{-}1)F(g)$$



	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



- With O_2 addition, [F] is increased and nitrogen forms NOF(g) and $NO_2F(g)$ which are stable volatile species.

[15] NIST-JANAF Thermo-chemical tables, 2012; [17] D. Linaschke, Proc. 23rd Eur. Photovoltaic Solar Energy Conf. Exhib. 2008

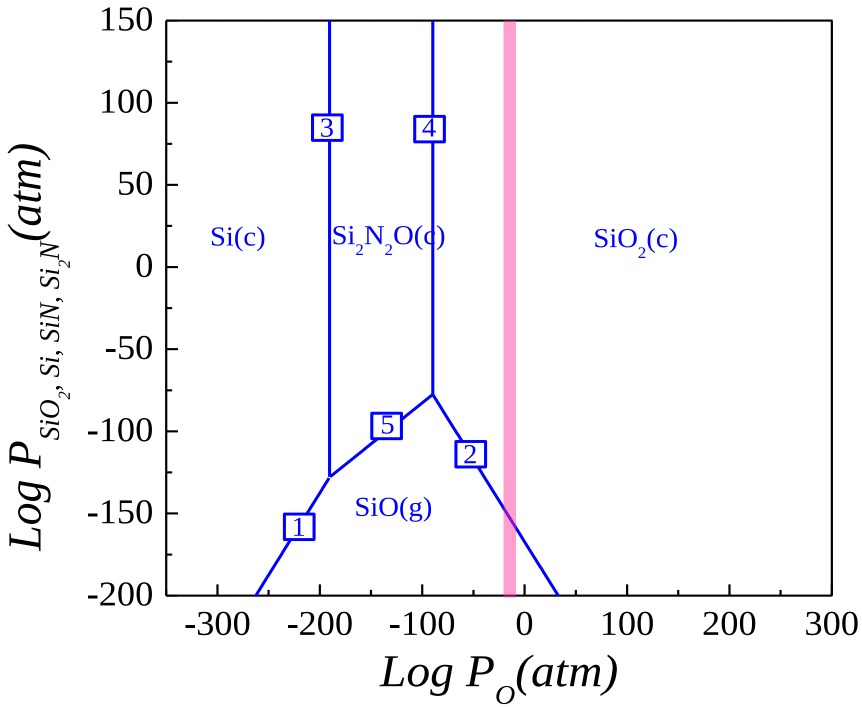
Surface of Si_3N_4-O & SiO_2-N

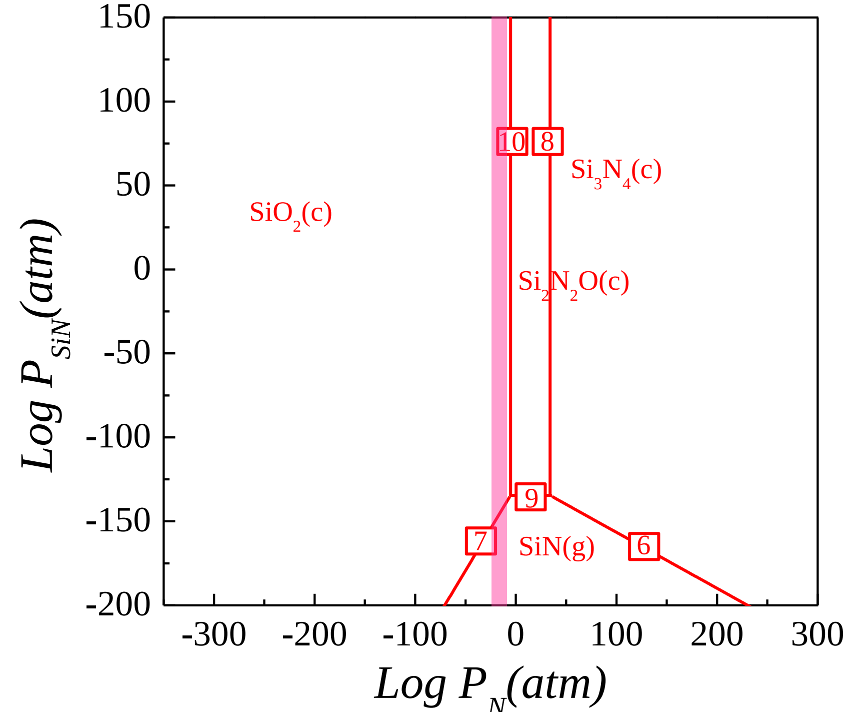
	ΔG(eV) [15]
SiO_2	-8.88
Si_3N_4	-6.66

Bond	Energy(eV) [16]
Si-O	4.69
Si-N	3.68

	Si_3N_4-O-300K	ΔG (eV)	log(K)
1	$Si(c) + O(g) \rightarrow SiO(g)$	-3.72	62.51
2	$SiO_2(c) \rightarrow SiO(g) + O(g)$	9.95	-167.16
3	$\frac{1}{2}Si_2N_2O(c) \rightarrow Si(c) + \frac{1}{2}N_2(g) + \frac{1}{2}O(g)$	5.67	-95.2
4	$\frac{1}{2}Si_2N_2O(c) + \frac{3}{2}O(g) \rightarrow SiO_2(c) + \frac{1}{2}N_2(g)$	-8.01	134.5
5	$\frac{1}{2}Si_2N_2O(c) + \frac{1}{2}O(g) \rightarrow SiO(g) + \frac{1}{2}N_2(g)$	1.95	-32.7

	SiO_2-N-300K	ΔG (eV)	log(K)
6	$\frac{1}{3}Si_3N_4(c) \rightarrow SiN(g) + \frac{1}{3}N(g)$	7.33	-123.2
7	$SiO_2(c) + N(g) \rightarrow SiN(g) + O_2(g)$	7.70	-129.3
8	$\frac{1}{2}Si_2N_2O(c) + \frac{1}{3}N(g) \rightarrow \frac{1}{3}Si_3N_4(c) + \frac{1}{4}O_2(g)$	0.658	-11.05
9	$\frac{1}{2}Si_2N_2O(c) \rightarrow SiN(g) + \frac{1}{4}O_2(g)$	8.01	-134.6
10	$SiO_2(c) + N(g) \rightarrow \frac{1}{2}Si_2N_2O(c) + \frac{3}{4}O_2(g)$	-0.32	5.3





- SiO_2(c) is the most stable species in both systems

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[15] NIST-JANAF Thermo-chemical tables, 2012; [16] Huheey, "The Strengths of Chemical Bonds," 1958

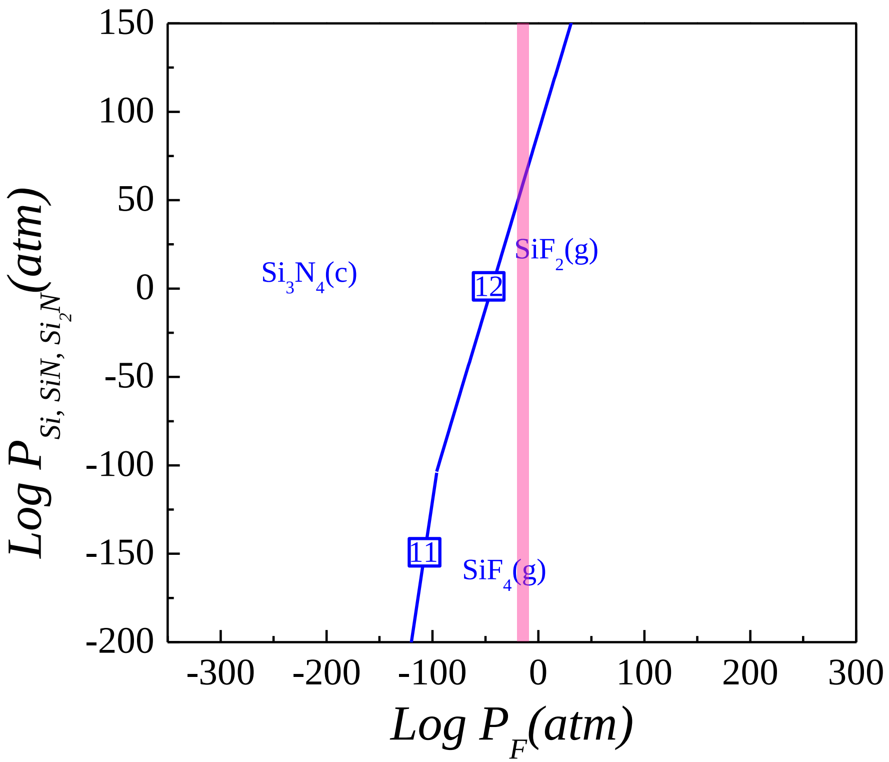
	ΔG(eV) [15]
SiF_4	-16.30
$SiOF_2$	-9.85

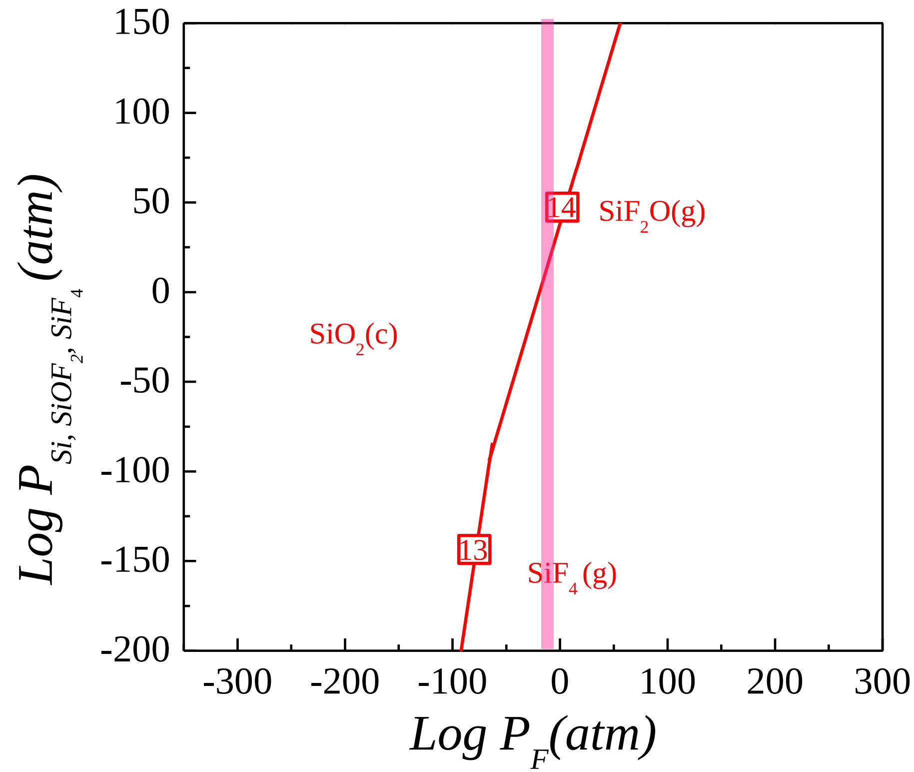
Surface of Si_3N_4-F & SiO_2-F

Bond	Energy(eV) [16]
Si-F	5.86

	Si_3N_4-F-300K	G(eV)	log(K)
11	$\frac{1}{3}Si_3N_4(c) + 4F(g) \rightarrow SiF_4(g) + \frac{2}{3}N_2(g)$	-16.66	279.8
12	$\frac{1}{3}Si_3N_4(c) + 2F(g) \rightarrow SiF_2(g) + \frac{2}{3}N_2(g)$	-5.27	88.5

	SiO_2-F-300K	G(eV)	log(K)
13	$SiO_2(c) + 4F(g) \rightarrow SiF_4(g) + O_2(g)$	-10.00	168.0
14	$SiO_2(c) + 2F(g) \rightarrow SiF_2O(g) + \frac{1}{2}O_2(g)$	-2.27	38.0





- The pressure of volatile products, SiF_2 and SiF_2O, are comparable in both systems

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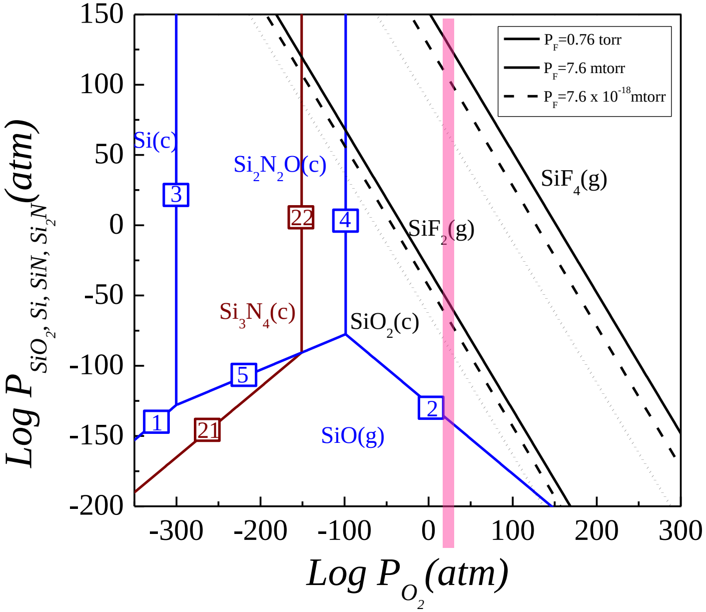
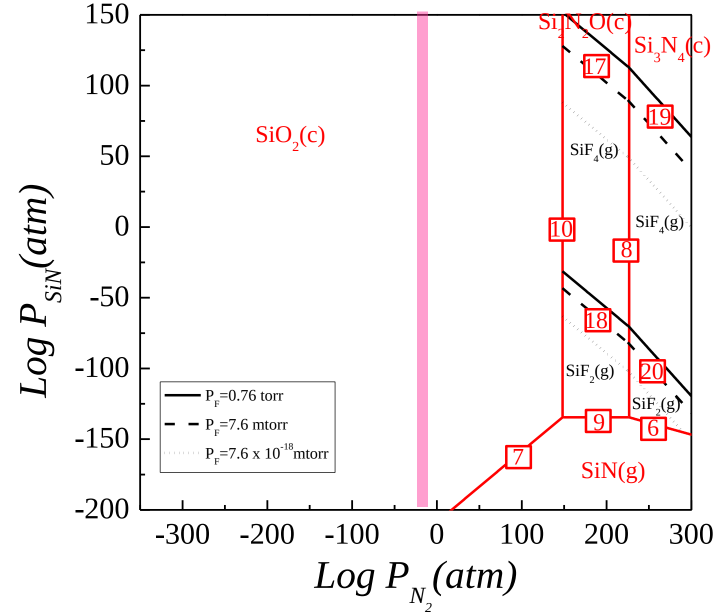
[15] NIST-JANAF Thermo-chemical tables, 2012; [16] Huheey, "The Strengths of Chemical Bonds," 1958

Surface of Si_3N_4-O_2-F & SiO_2-N_2-F

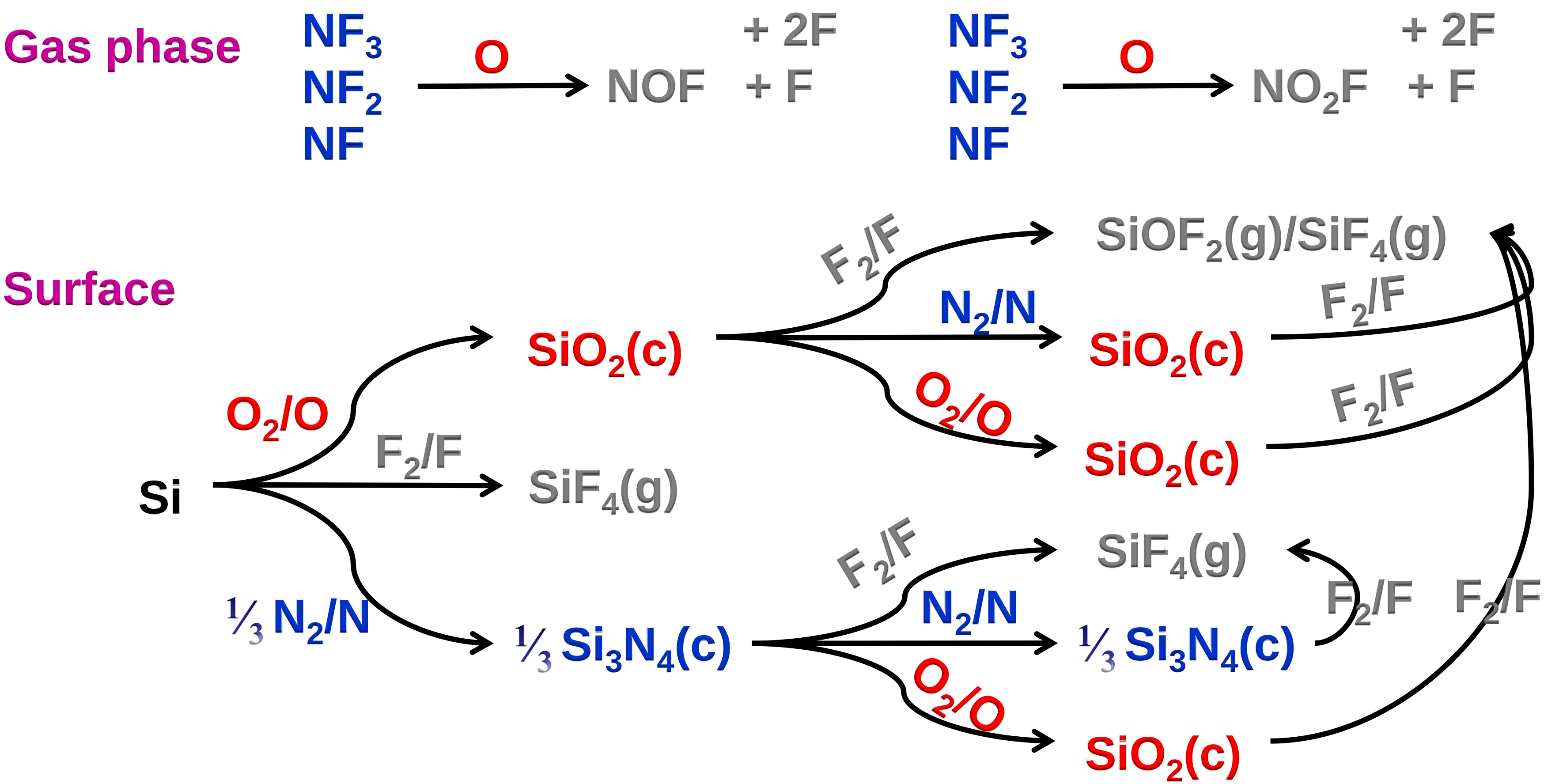
	Si_3N_4-O_2-F-300K	G (eV)	log(K)		SiO_2-N_2-F-300K	G (eV)	log(K)
1	$Si(c) + \frac{1}{2}O_2(g) \rightarrow SiO(g)$	-1.32	22.0	6	$\frac{1}{3}Si_3N_4(c) \rightarrow SiN(g) + \frac{1}{3}N_2(g)$	5.76	-96.8
2	$SiO_2(c) \rightarrow SiO(g) + \frac{1}{2}O_2(g)$	7.56	-126.5	7	$SiO_2(c) + \frac{1}{2}N_2(g) \rightarrow SiN(g) + O_2(g)$	12.42	-208.6
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	8	$\frac{1}{2}Si_2N_2O(c) + \frac{1}{6}N_2(g) \rightarrow \frac{1}{3}Si_3N_4(c) + \frac{1}{4}O_2(g)$	2.25	-11.3
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	9	$\frac{1}{2}Si_2N_2O(c) \rightarrow SiN(g) + \frac{1}{4}O_2(g)$	8.01	-134.6
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	10	$SiO_2(c) + \frac{1}{2}N_2(g) \rightarrow \frac{1}{2}Si_2N_2O(c) + \frac{3}{4}O_2(g)$	4.41	-74.1
15	$SiO_2(c) + 4F(g) \rightarrow SiF_4(g) + O_2(g)$	-10.00	168.0	17	$\frac{1}{2}Si_2N_2O(c) + 4F(g) \rightarrow SiF_4(g) + \frac{1}{2}N_2(g)$	-14.41	242.0
16	$SiO_2(c) + 2F(g) \rightarrow SiF_2(g) + O_2(g)$	1.39	-23.0	18	$\frac{1}{2}Si_2N_2O(c) + 2F(g) \rightarrow SiF_2(g) + \frac{1}{2}N_2(g)$	-3.02	50.8
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	19	$\frac{1}{3}Si_3N_4(c) + 4F(g) \rightarrow SiF_4(g) + \frac{2}{3}N_2(g)$	-16.66	279.8
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	20	$\frac{1}{3}Si_3N_4(c) + 2F(g) \rightarrow SiF_2(g) + \frac{2}{3}N_2(g)$	5.27	-88.5





- Si_3N_4(c) could be oxidized by O_2(g) and then be removed by F.

Summary



- The addition of O_2 increase significantly the [F]
- The removal rate of SiO_2(c) and Si_3N_4(c) by F are comparable
- NF_3 could replace the SF_6 with O_2 addition.

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Future Plans

Next Year Plans

- **Identify potential low impact gases in target applications**
- **Perform thermodynamic calculations to assess potential impact and projected effectiveness**
- **Implement target chemistries and carry out plasma etching assessment**

Long-Term Plans

- **Formulate the models to predict emission from plasma processes**
- **Assess the effectiveness of the plasma chemistries compared to that of the PFC gases**

Publications, Presentations, and Recognitions/Awards

- **Presentation in Gordon Research Conference(GRC), July 2012**
- **Invited talk to AVS International Symposium, October 2012**

Industrial Interactions and Technology Transfer

- **Video conference to Intel, January 31, 2012 (Karson Knutson, Doosik Kim)**
- **Conference call with Novellus, March 2012 (Ron Powell, Roey Shaviv, Juwen Gao)**
- **Student interview at IBM, February 29, 2012**
- **Student interview with Intel, March 2012**
- **SRC Industrial Liaison, Satyarth Suri at Intel, April 2012**
- **ERC Webinar, June 2012**
- **Student will have poster in Gordon Research Conference, July, 2012**
- **Conference call with Intel, September 2012 (Satyarth Suri, Bob Turkot)**

→ ***After studying the TSV by detailed thermodynamic analysis, the following research is kinetic measurements.***