Non-PFC Plasma Chemistries for Patterning Complex Materials/Structures

(*Task Number: 425.038*)

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Objectives

- **Assess the thermodynamic feasibility of patterning etch-resistant materials (complex materials and structures)**

- **Identify the non-PFC alternative for priority test cases (such as through silicon via etch and magnetic metal etch)**

- **Validate the theoretical assessment by performing etching experiments of these materials with industrial sponsors**

ESH Metrics and Impact

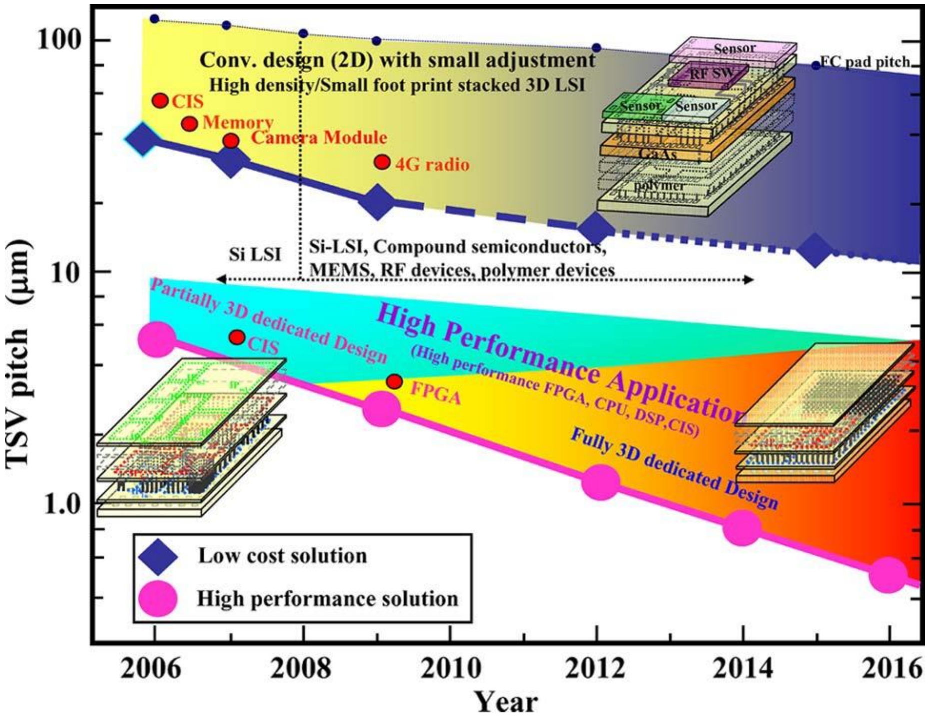
1. **Reduction in the use of PFC gases by focusing on non-PFC chemistries**

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

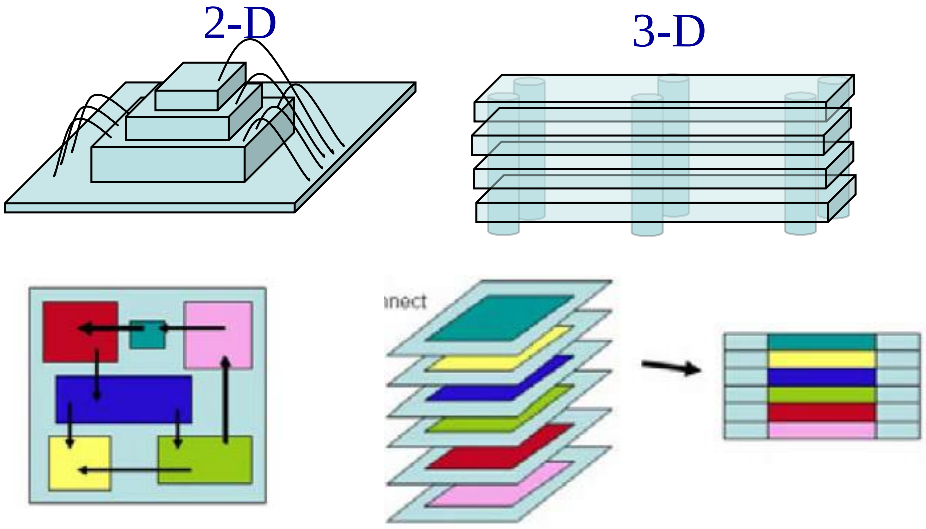
3. **Reduction in the use of chemicals by tailoring the chemistries to the specific materials to be removed**

TSV (Through Silicon Via)

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



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



Advantages:

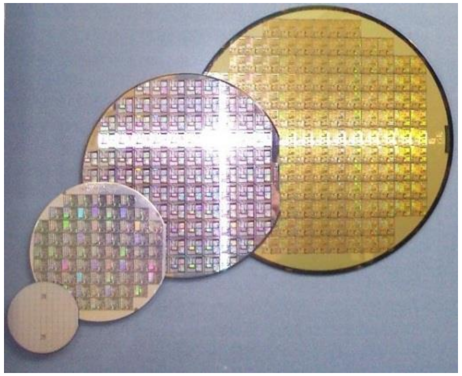
- Smaller footprint and form-factor
- Less weight and power consumption
- Potentially lower cost

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

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

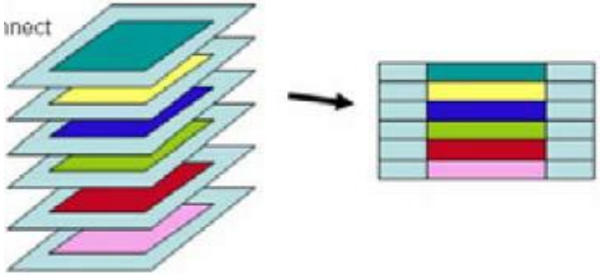
Challenges in TSV

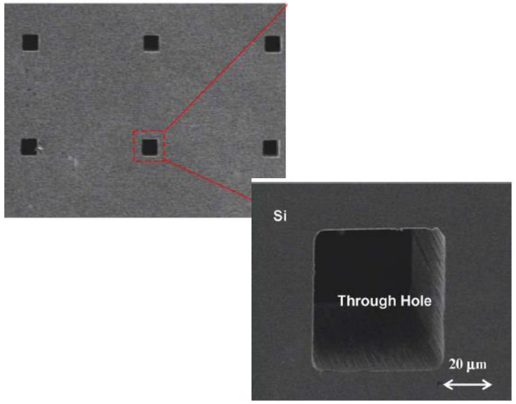
High etch rate (~1 µm/min)



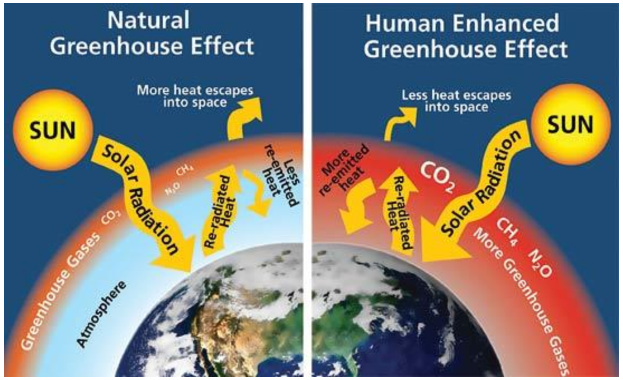
Silicon size (inch)	Thickness (um)
6	**675**
8	**725**
12	**775**
18	**925**

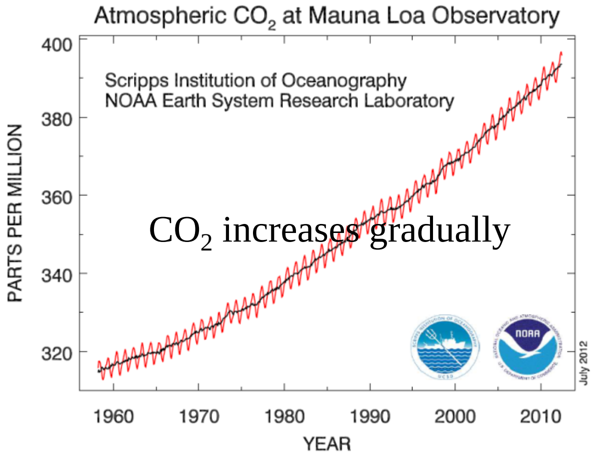
High aspect ratio (>10) [1, 2]





Greenhouse gas usage [3]



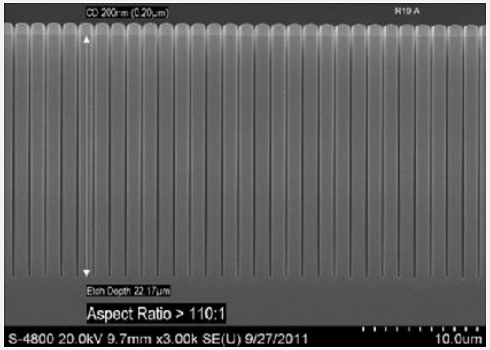
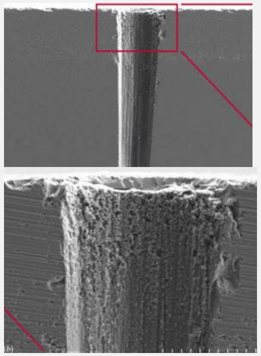


CO_2 increases gradually

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

[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

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.

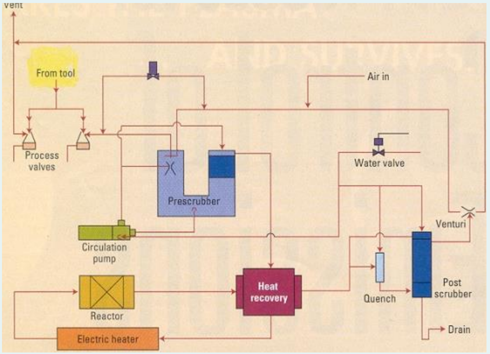
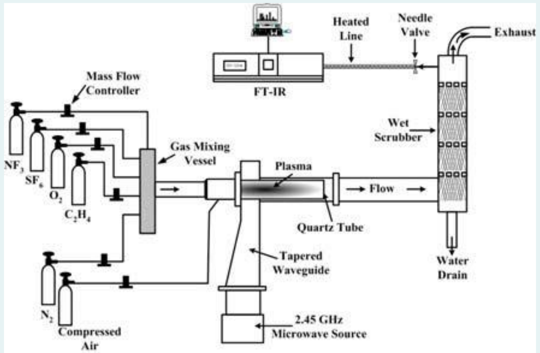
[10] United Nations Environment Program(UNEP), 2010; [11] W. Tsai, J Hazard Mater, 2008

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 Proc. Sys.	Catalytic Decomposition Systems	Plasma Abatement Systems
		
Not effective in decomposing CF_4	The catalyst lifetime only 18 months	For semiconductor industry in plasma etching process and chamber cleaning

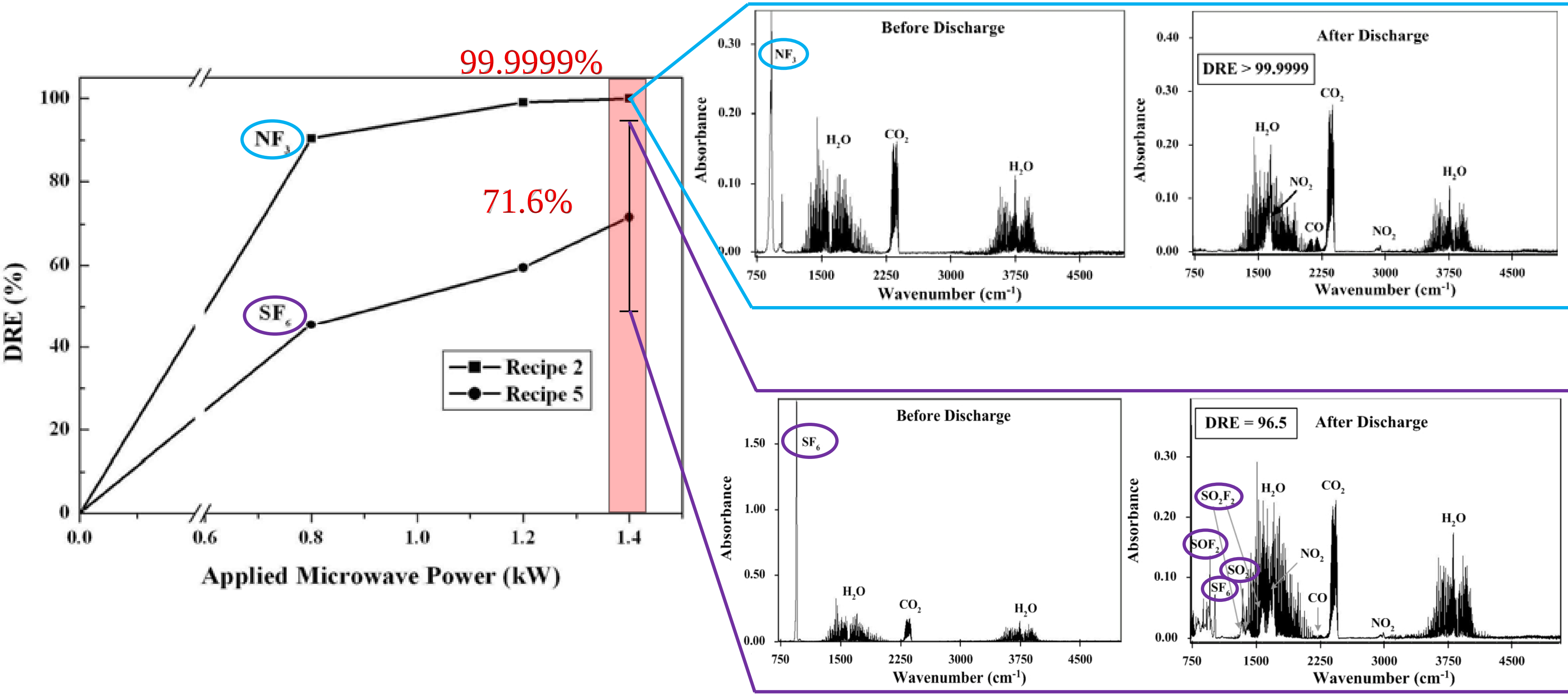
SRC Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

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

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

Plasma Torch Abatement of NF_3 & SF_6[13]

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



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

→ Byproduct such as HF could be removed by scrubbing [13,14]

[13] Yong C. Hong, IEEE, 2005; [14] M.J. de Wild-Scholten, 22nd European Photovoltaic Solar Energy Conference, 2007

Etch Rate of 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]

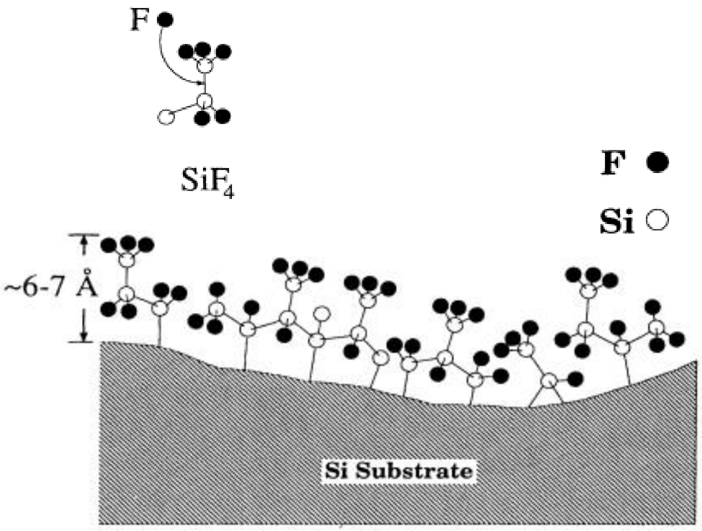
* :poly-silicon

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

	Reactions	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**

	Reactions	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]

	Reactions	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 from thermal 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

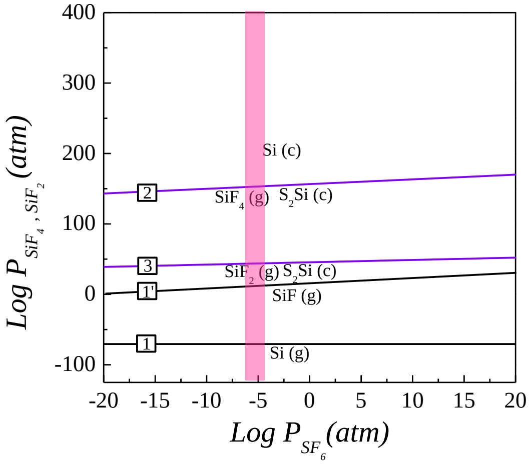
Can SF_6 be Replaced by NF_3?

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

$\Delta G = -7.0eV$

$\Delta G = - 1.9eV$

	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

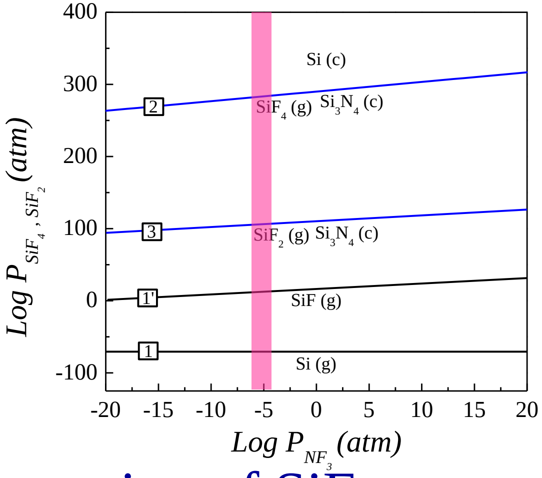


$Si + \frac{2}{3} NF_3(g) \rightarrow \frac{1}{2} SiF_4(g) + \frac{1}{6} Si_3N_4(c) + 4F(g) \rightarrow \frac{1}{2} SiF_4(g) + \frac{2}{3} NF_3(g)$

$\Delta G = -8.6eV$

$\Delta G = -0.2eV$

	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

A Strategy to Remove Si_3N_4 by O_2 Addition

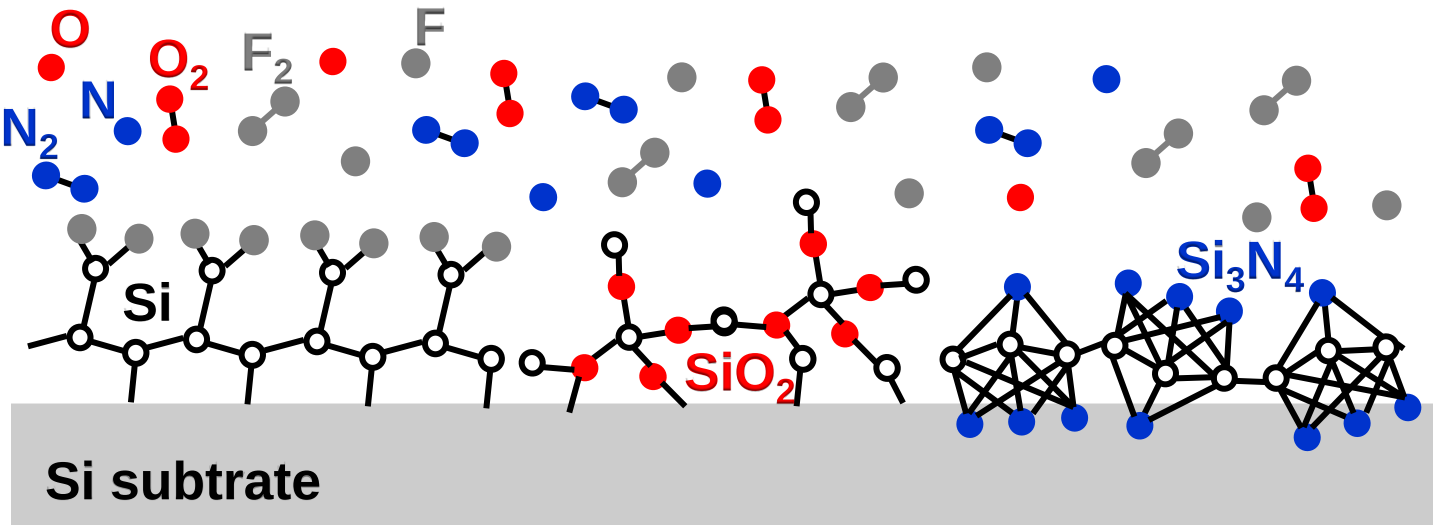
Formation of $Si_3N_4(c)$	ΔG(eV)
$Si(c) + \frac{2}{3}NF_3(g) \rightarrow \frac{1}{2}SiF_4(g) + \frac{1}{6}Si_3N_4(c)$	-8.6

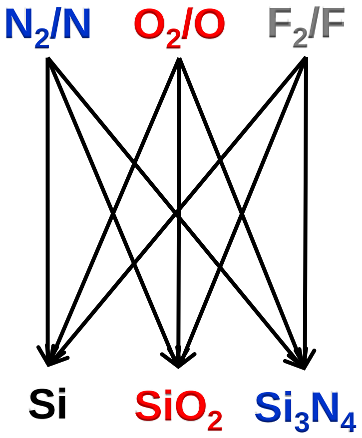
Removal of $Si_3N_4(c)$ by F	ΔG(eV)
$\frac{1}{6}Si_3N_4(c) + 4F(g) \rightarrow \frac{1}{2}SiF_4(g) + \frac{2}{3}NF_3(g)$	-10.2

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

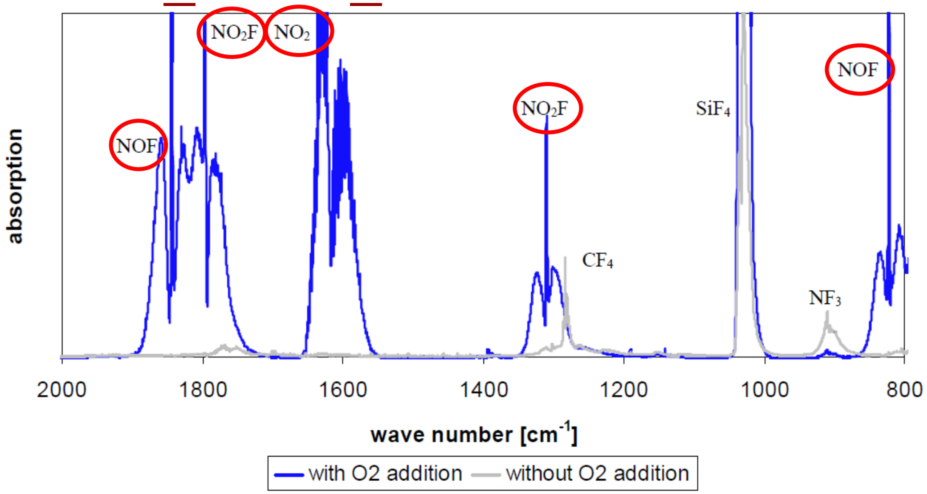
- The interaction of N/O/F need to be determined

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



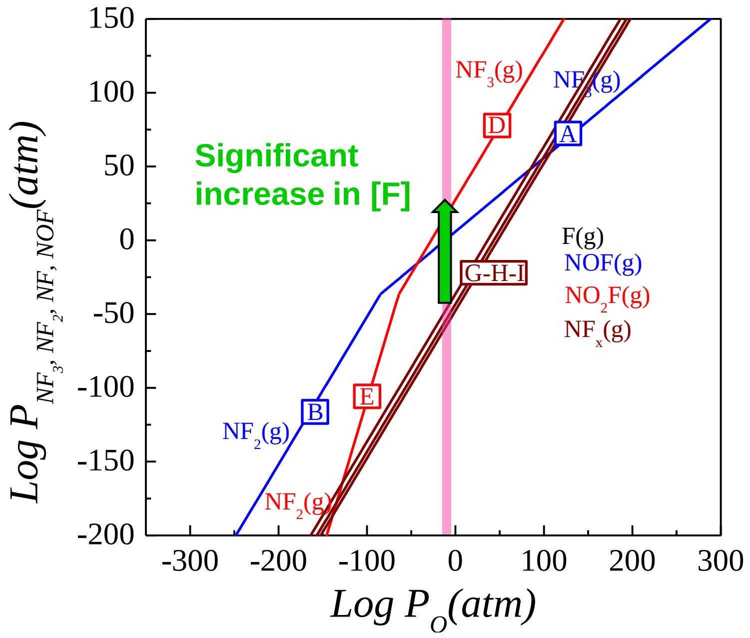
- From the FTIR of NF_3/O_2 silicon etching[17], $NO_2F(g)$, NOF(g) and NO(g) can be found when the NF_3 with O_2 addition.
- The following reactions have been proposed,

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

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

	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



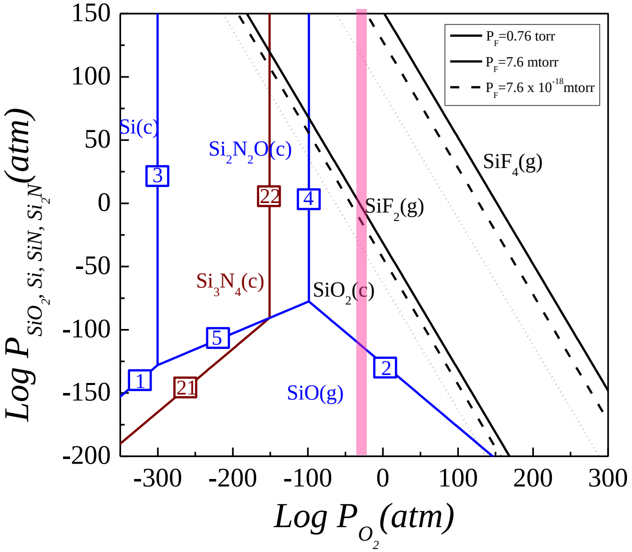
- With O_2 addition, [F] is increased and nitrogen forms NOF(g) and $NO_2F(g)$ which are stable volatile species.

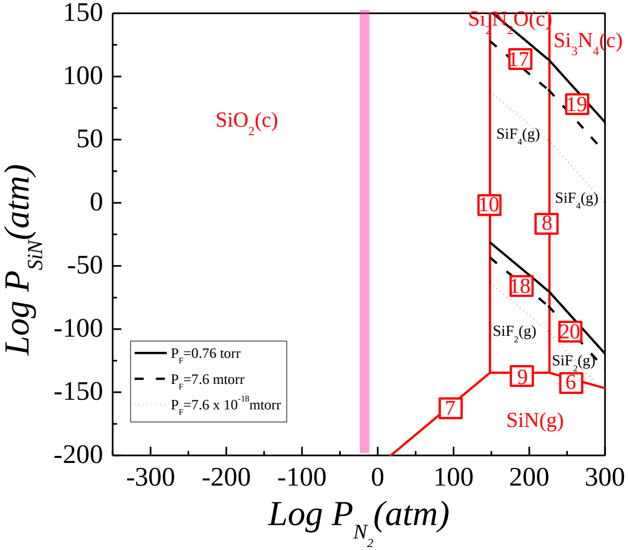
[15] NIST-JANAF Thermo-chemical tables, 2012; [17] D. Linaschke, Proc. 23rd Eur. Photovoltaic Solar Energy Conf. Exhib. 2008

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

	Si_3N_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

	SiO_2-N_2-F-300K	G (eV)	log(K)
6	$\frac{1}{3}Si_3N_4(c) \rightarrow SiN(g) + \frac{1}{3}N_2(g)$	5.76	-96.8
7	$SiO_2(c) + \frac{1}{2}N_2(g) \rightarrow SiN(g) + O_2(g)$	12.42	-208.6
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
9	$\frac{1}{2}Si_2N_2O(c) \rightarrow SiN(g) + \frac{1}{4}O_2(g)$	8.01	-134.6
10	$SiO_2(c) + \frac{1}{2}N_2(g) \rightarrow \frac{1}{2}Si_2N_2O(c) + \frac{3}{4}O_2(g)$	4.41	-74.1
17	$\frac{1}{2}Si_2N_2O(c) + 4F(g) \rightarrow SiF_4(g) + \frac{1}{2}N_2(g)$	-14.41	242.0
18	$\frac{1}{2}Si_2N_2O(c) + 2F(g) \rightarrow SiF_2(g) + \frac{1}{2}N_2(g)$	-3.02	50.8
19	$\frac{1}{3}Si_3N_4(c) + 4F(g) \rightarrow SiF_4(g) + \frac{2}{3}N_2(g)$	-16.66	279.8
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

→ Si_3N_4 spacer etch selectivity → tomorrow morning's tutorial

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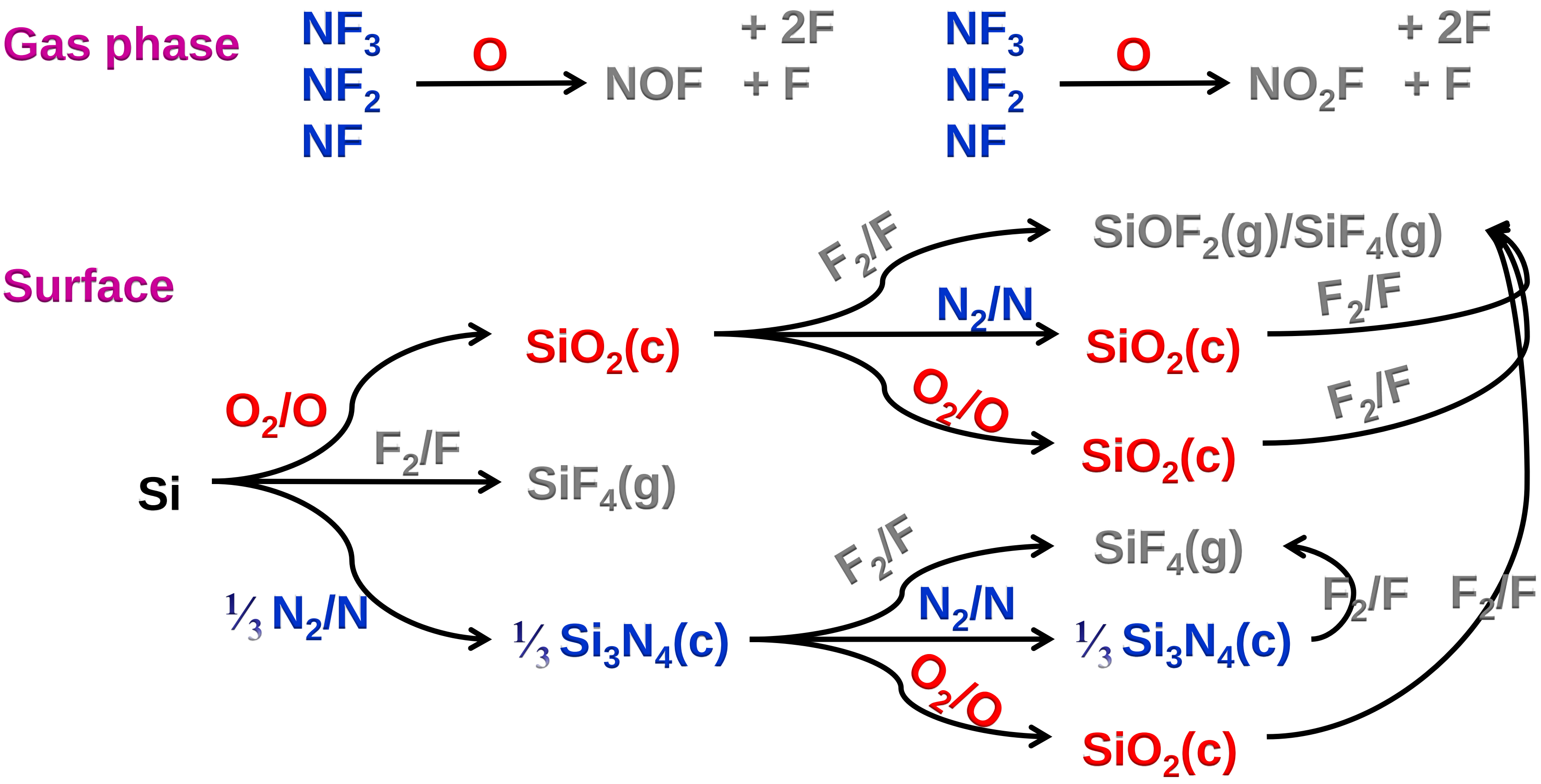
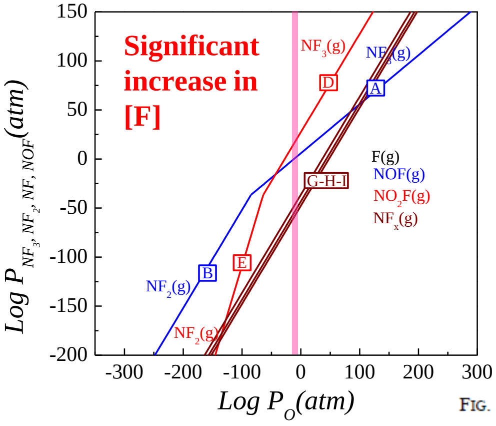
Summary of Pathway



- 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.

Proposed TSV Experiments

Amount of F radical [This work]
=f(The amount of oxygen introduction)



Etch rate of poly-Si
=f(power, NF3 flow rate) [2]

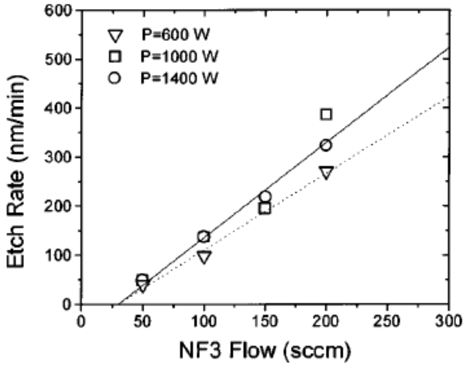


FIG. 2. Etch rates of poly-Si vs NF_3 flow at varied microwave p

Etch rate of Si
=f(O2/NF3) [2]
RF=1400W P=1mtorr

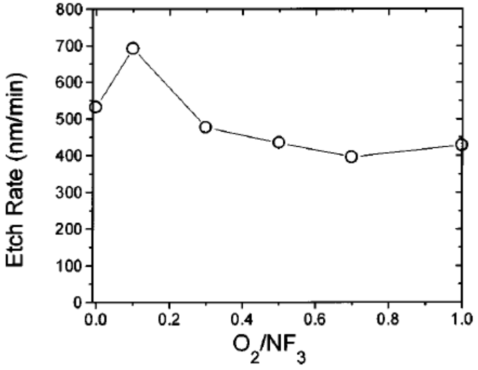
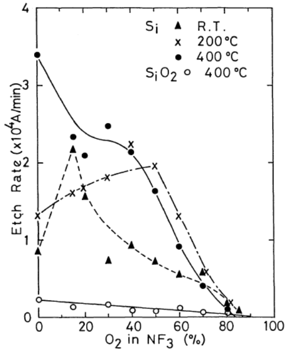


FIG. 4. Poly-Si etch rates vs O_2 content in a NF_3 discharge.

Etch rate of Si
=f(O2/NF3) [3]
RF=30W P=500mtorr



ig. 5. Etch rate of Si as a function of O_2 concentration in NF_3 for various etching temperatures together with SiO_2 etch rate at an etching temperature of 400°C.

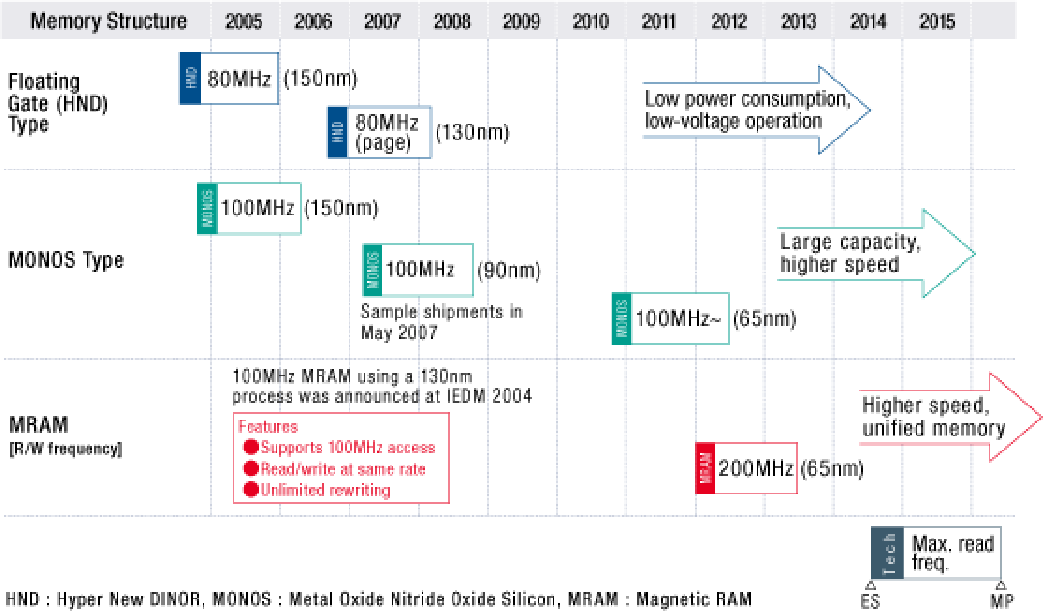
The plasma condition of NF_3/O_2 could be comparable to what was used in SF_6 chemistry (the proposed conditions are shown).

Gas comp. / Op. pressure	O_2 7% $NF_3$93%	O_2 10% $NF_3$90%	O_2 13% $NF_3$87%
1mtorr	√	√	Δ
100mtorr	Δ	√	Δ
500mtorr	Δ	√	√

1. B. E. E. Kastenmeier, P. J. Matsuo, G. S. Oehrlein, and J. G. Langan, J. Vac. Sci. Technol. A 16, 2047 (1998)
2. P. J. Matsuo, B. E. E. Kastenmeier, G. S. Oehrlein, and J. G. Langan, J. Vac. Sci. Technol. A 17, 2431 (1999)
3. A. Nagata, H. Ichihashi, Y. Kusunoki, and Y. Horiike, Jpn. J. Appl. Phys., Part 1 28, 2368 (1989)

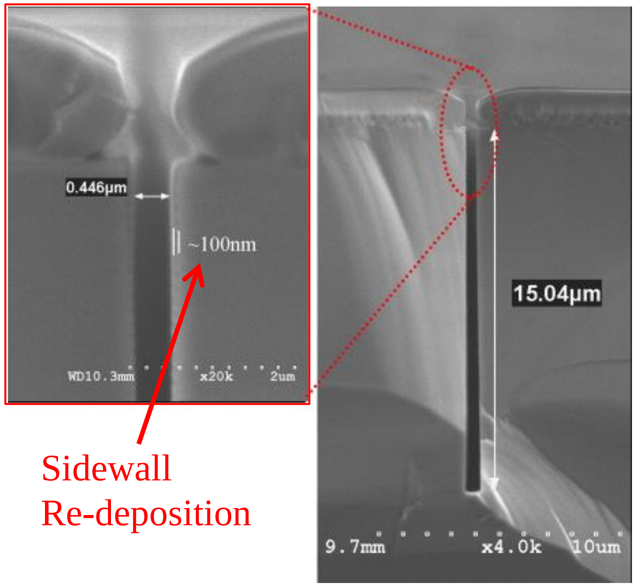
Magnetic Devices Materials

Memory overview [RENASES]



HND : Hyper New DINOR, MONOS : Metal Oxide Nitride Oxide Silicon, MRAM : Magnetic RAM

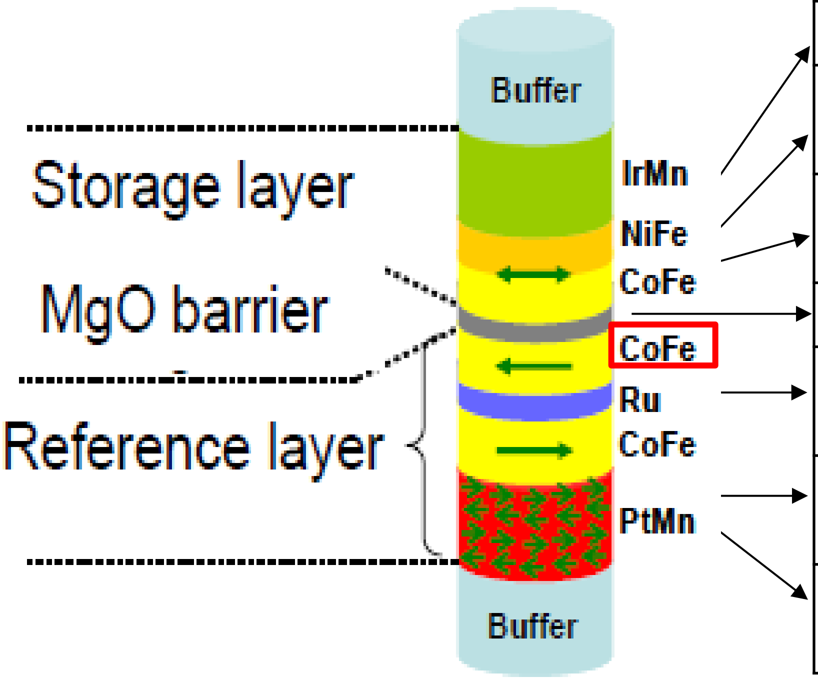
Redeposition in high aspect ratio features [Reza Abdolvand, 2008]



Aspect Ratio ~40

- MRAM can be the solution to the memory bottle neck
- MRAM patterning is challenging due to the materials of choice and the high aspect ratio of cells

Potential Target Material in MRAM



Material	Chemistry	Reference
Ni	CO/NH_3	Matsui, 2002
Fe	Ar/O_2 CH_3OH	Cardoso, 2001 Kinoshita, 2010
Co	Ar Ar	Braganca, 2009 Okamura, 2005
MgO	CH_3OH/Ar	Kim, 2012
Ru	CF_4/O_2 Ar	Yen, 2006 Persson, 2011
PtMn PtMn	CH_3OH Cl_2	Otani, 2007 Kumagai, 2004
Mn	BCl_3/Ar SF_6/Ar	Hong, 1999 Hong, 1998

- Problem of etch resistance compounded by need for selectivity in increasingly complex stacks
- For a systematic approach, the work starts with simple metals (Fe, Co, Ni)

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**

The Need for Thermodynamic Data

- **If thermodynamic parameter is not available,**

DFT calculation

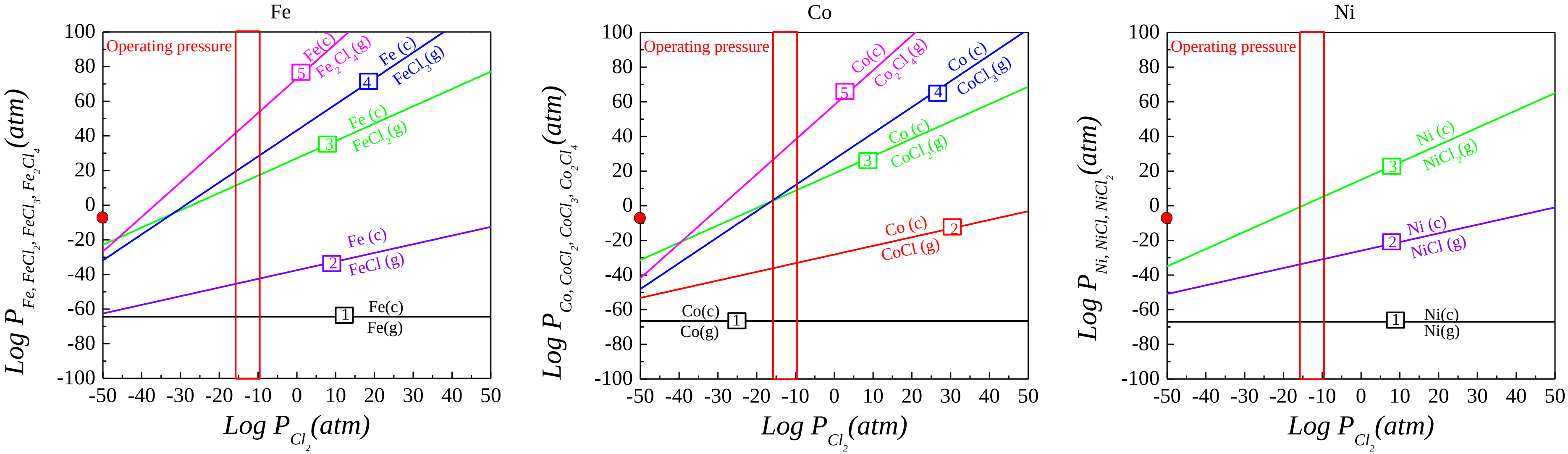
- Simulation program : Gaussian
- Examples for DFT calculation
- ΔH_f and ΔH_{rxn} could be calculated
- However, Gaussian is not good for calculating a large system with many metal atoms, so MD calculation is needed for accuracy

MD calculation

- Simulation program : DLPOLY
- System for simulation :

  ML_2, ML_3 (M=Co, Ni, Fe), L: organic ligand. (a system comprised of 125 metal atoms)
- ΔH_{vap} could be calculated

Volatility Diagram: M-Cl$_2$

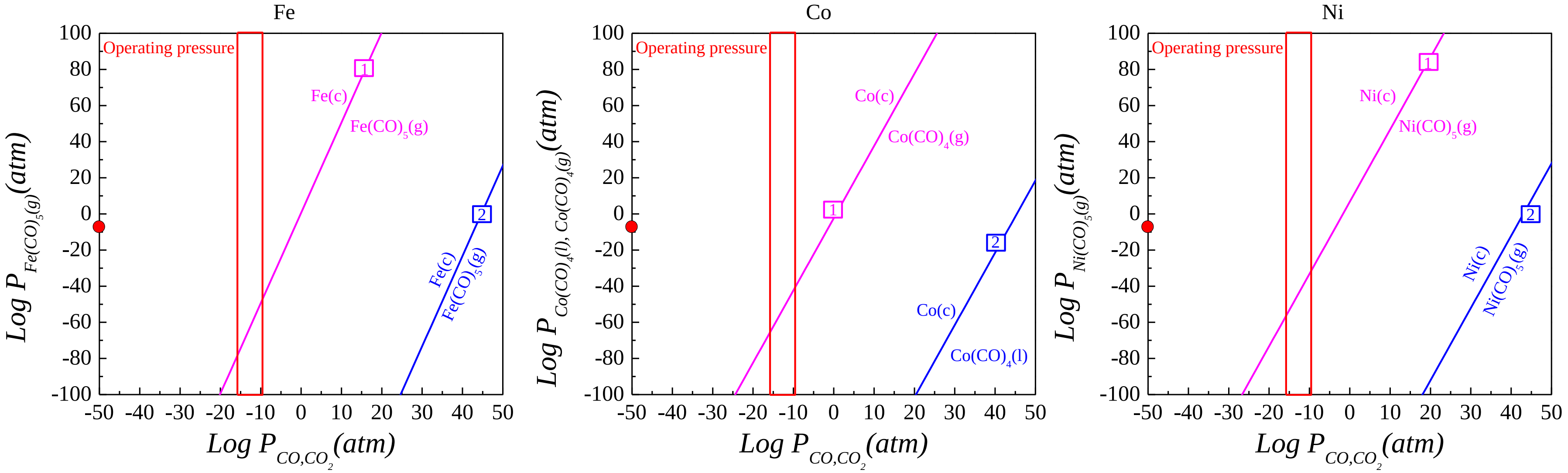


	Reation_ΔG(kJ/mol)	Fe	Co	Ni
1	**M**(c) → **M** (g)	369.8	382.1	384.7
2	**M** + 1/2Cl$_2$(g) → **M**Cl(g)	215.6	161.9	149.1
3	**M** + Cl$_2$(g) → **M**Cl$_2$ (g)	-155.6	-107.2	-86.2
4	**M** + 3/2Cl$_2$(g) → **M**Cl$_3$ (g)	-247.8	-154.5	x
5	**M** + 2Cl$_2$(g) → **M**$_2$Cl$_4$ (g)	-420.5	-334.0	x
	x=unstable product			

- Volatility of chlorinated products: FeCl$_x$>NiCl$_x$>CoCl$_x$

NIST-JANAF Thermo-chemical tables, 2012

Volatility Diagram: Metal-(CO) Complex



	Reation ΔG(kJ/mol)	Fe	Co	Ni
1	**M**(c) + xCO(g) → **M** $(CO)_x$(g)	-3.4	13.6	-38.7
2	**M**(c) + xCO_2(g) → **M** $(CO)_x$(g) + yO_2 (g)	1282.7	1042.5	990.2

Fe, Ni: x=5, y=2.5; Co: x=4, y=2

- Volatility of M-$(CO)_x$ complexes: $Ni(CO)_5 > Fe(CO)_5 > Co(CO)_4$

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S.J. Pearton, Mat. Res. Soc. Symp. Proc. 2000

Fe, Co, Ni Etch Rate in CO/NH_3

Etch rate (nm/min) Etchant	NiFeCo	NiFe	CoFe	CoFe B	Power (W)	Pressure (mtorr)	Ref
Cl_2/Ar		>100			700	2	[r]
BI_3/Ar		50			700	2	[r]
ICl/Ar		50			700	2	[r]
IBr/Ar		50			700	2	[r]
CO(12%)/NH_3	48	50			700	2	[r]
NH_3(100%)	22	20			700	2	[r]
BBr_3/Ar		20			700	2	[r]
CH_4(7%)/H_2(27%)/Ar		<10			700	2	[r]
SF_6/Ar		<10			700	2	[r]
CO(100%)	-6(dep.)	-8(dep)			700	2	[r]
CO(50%)/NH_3		125	70		280	2.6	[s]
CO(50%)/NH_3		90			300	6	[t]
NH_3(100%)		70			300	6	[t]
CO(33%)/NH_3				12	700	5	[u]
NH_3(100%)				4	700	5	[u]
Cl_2(66%)/Ar(33%)		560			150	1.5	[v]
Ar(100%)		280			150	1.5	[v]
Cl_2(66%)/H_2(33%)		200			150	1.5	[v]
CH_4(7%)/H_2(27%)/Ar		80			150	1.5	[v]
Ar(100%)				43	800	5	[w]
CH_3OH(20%)/Ar				15	800	5	[w]

- The etch rate: Halogen/Ar > CO/NH_3 > NH_3 > CO

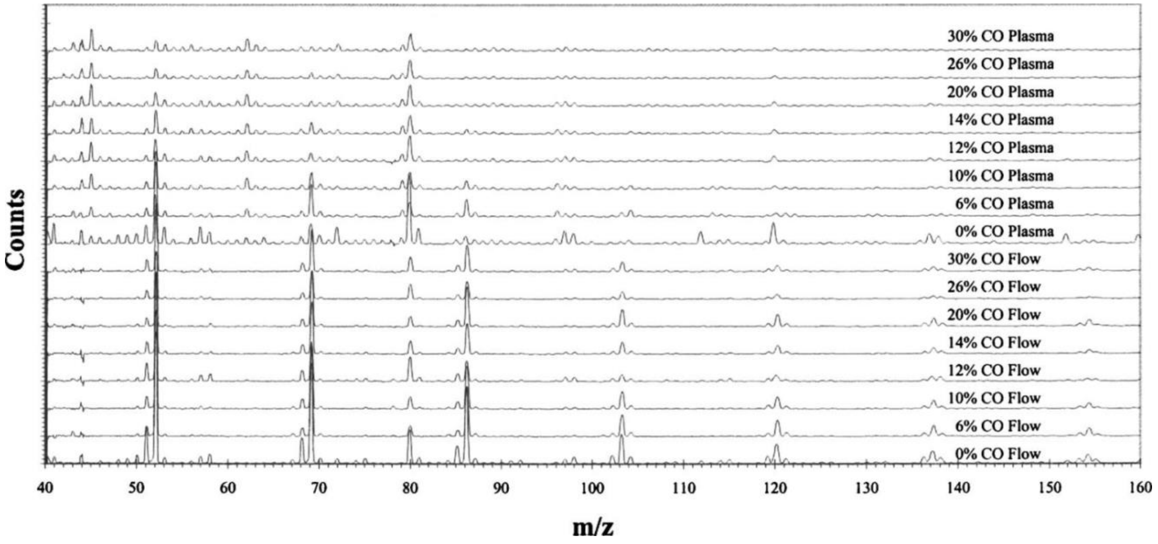
[r] S.J. Pearton, Mat. Res. Soc. Symp. Proc. 2000; [s] H. Kubota, J. Magn. Magn. Mater., 2004; [t] N. Matsui, J Vacuum, 2002; [u] J. Park, J. Electrochem. Soc. , 2011

[v] K. B. Jung, Appl. Phys. Lett. 1997;[w] Y. Xiao, Thin Solid Film, 2011

CO/NH_3 Plasma Species[1]

Table 1. The main products in CO/NH_3 Plasma Mass spec.

m/z	species
45	$HCONH_2$ (Formamide)
52	$(NH_3)_3H^+$
62	$(HCONH_2)(NH_3)H^+$
69	$(NH_3)_4H^+$
80	$(HCONH_2)(NH_3)_2H^+$



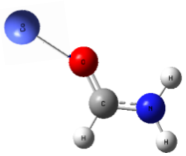
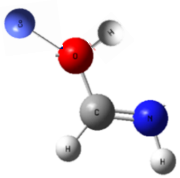
- The mass spectrometry of CO/NH_3 has been studied, the main species generated in the plasma are listed in the table. [1]
- It's difficult to confirm the formation of metal complexes such as the low flux of products off of the metal surface and cracking during the ionization.

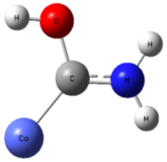
[1] A. Orland, J. Vac. Sci. Technol. B 23, 2005

$\Delta_f H$ of M-CH_3NO Complexes

Method: DFT(B3LYP) T=298.15K
Basis set:6-311G+ P=1atm

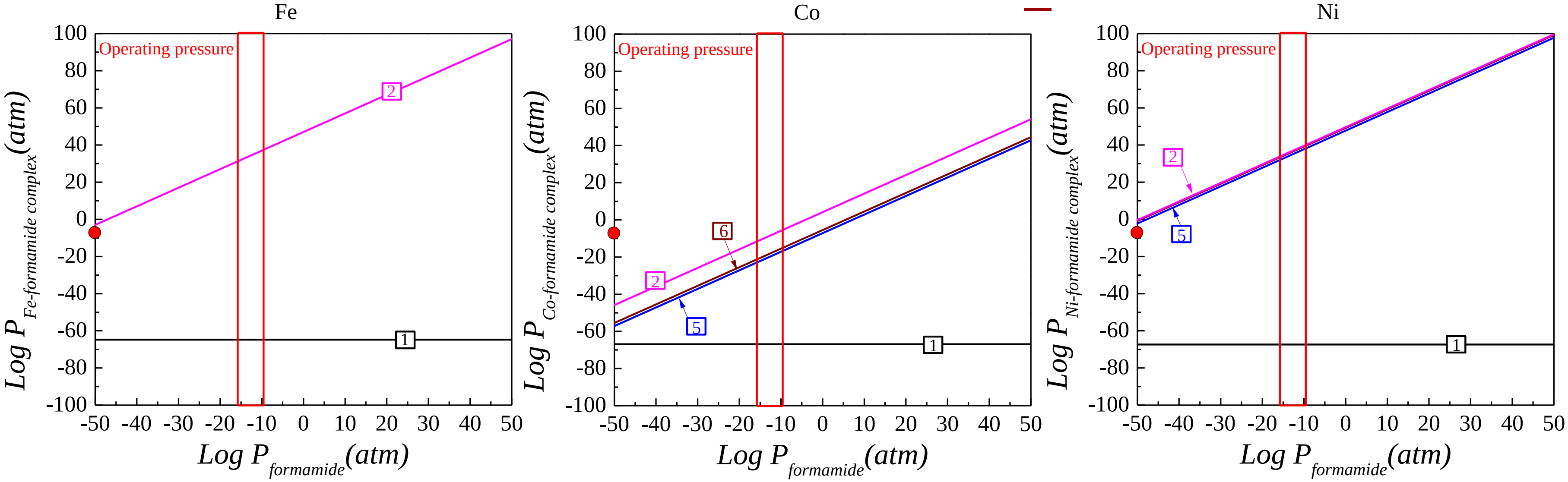
$\Delta_f H$(kJ/mol)	[MCH_3NO]	[MCH_3NO]	[MCH_3NO]	[MCH_3NO]
Fe	-76.2	x	x	x
Co	x	240.4	240.8	228.7
Ni	-76.8	x	-71.4	-77.9
x=unstable product				

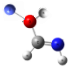
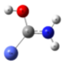





- Although the Fe, Co, Ni-formamide complexes are not available in the literature, the structure of Ca-formamide complex has been simulated by Gaussian
- Volatility of complexes: Fe-CH_3NO ~ Ni-CH_3NO > Co-CH_3NO

Volatility Diagram: M-CH_3NO Complex

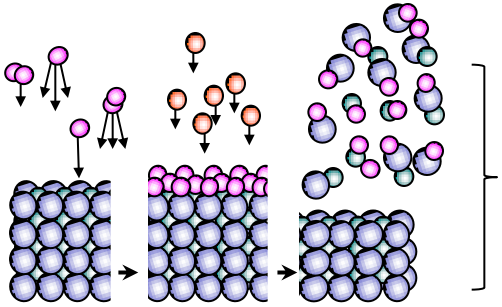


	Reation_ΔG(kJ/mol)	Fe	Co	Ni
1	**M**(c) → **M**(g)	369.8	382.1	384.7
2	CH_3NO(g) +**M**(g)→ 	-268.4	-23.7	-283.3
4	CH_3NO(g) +**M**(g)→ 	x	56.3	x
5	CH_3NO(g) +**M**(g)→ 	x	40.4	-272.5
6	CH_3NO(g) +**M**(g)→ 	x	40.9	-280.6

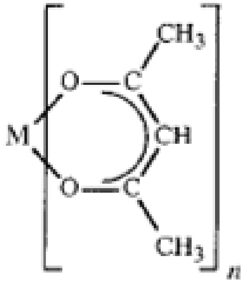
- Volatility of complexes: Fe-CH_3NO>Ni-CH_3NO>Co-CH_3NO

NIST-JANAF Thermo-chemical tables, 2012

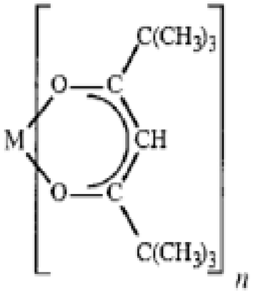
Other Potential Chemistries



Atomic Layer Etching



Acetylacetonate (ACAC)



2,2,6,6-tetra-methyl-3,5-heptanedionate (TMHD)

Product	MP	BP
$CoCl_2$	737	1049
$CoCO_3$	**280***	
$Co_2(CO)_8$	**51***	
$Co_4(CO)_{12}$	**60***	
$Co(acac)_2$	170	181 (exp~200)
$Co(acac)_3$	211	170 (exp~190)
$Co(tmhd)_2$	254	171 (exp~192)
$Co(tmhd)_3$	143	161 (exp~179)
$FeCl_3$	308	~316
$Fe(C_5H_5)_2$	172.5	249
$Fe(CO)_4H_2$	-70	-20*
$Fe(CO)_5$	**-20.5**	**103**
$Fe_2(CO)_9$	**100***	
$Fe_3(CO)_{12}$	**140**	
$Fe(acac)_3$	184	161 (exp~182)
$Fe(tmhd)_3$	164	150 (exp~177)
$NiCl_2$	1031	985 (subl)
$Ni(CO)_4$	**-19**	**42 (exp~60)**

- “Reverse engineering” of ALD points to organometallic chemistry as a viable alternative to halogens

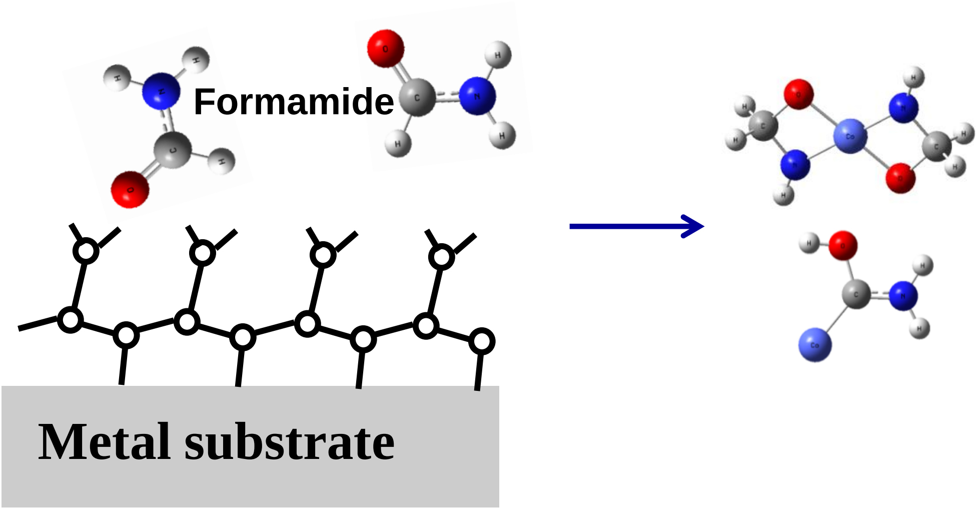
NIST-JANAF Thermo-chemical tables, 2012

Summary of Fe, Co, Ni Etching

- Fe complex has higher volatility compare to Co and Ni
- Some of the complex products are stable which implies potential etch product in CO/NH_3 plasma treatment
- The existence of metal-formamide complexes have been confirmed, the reactions between the metal cluster and formamide need to be calculated by MD simulation

Table 1. The main products in CO/NH_3 Plasma Mass spec.

m/z	**species**
45	$HCONH_2$ (Formamide)
52	$(NH_3)_3H^+$
62	$(HCONH_2)(NH_3)H^+$
69	$(NH_3)_4H^+$
80	$(HCONH_2)(NH_3)_2H^+$



Reference

- c. Jansen, H., et al., The Black Silicon Method - a Universal Method for Determining the Parameter Setting of a Fluorine-Based Reactive Ion Etcher in Deep Silicon Trench Etching with Profile Control. Journal of Micromechanics and Microengineering, 1995. 5(2): p. 115-120.
- d. Mansano, R.D., P. Verdonck, and H.S. Maciel, Deep trench etching in silicon with fluorine containing plasmas. Applied Surface Science, 1996. 100: p. 583-586.
- e. Yeom, G.Y., Y. Ono, and T. Yamaguchi, Polysilicon Etchback Plasma Process Using Hbr, Cl2, and Sf6 Gas-Mixtures for Deep-Trench Isolation. Journal of the Electrochemical Society, 1992. 139(2): p. 575-579.
- f. Matsuo, P.J., et al., Role of N-2 addition on CF4/O-2 remote plasma chemical dry etching of polycrystalline silicon. Journal of Vacuum Science & Technology a-Vacuum Surfaces and Films, 1997. 15(4): p. 1801-1813.
- g. Syau, T., B.J. Baliga, and R.W. Hamaker, Reactive Ion Etching of Silicon Trenches Using Sf6/O-2 Gas-Mixtures. Journal of the Electrochemical Society, 1991. 138(10): p. 3076-3081.
- h. Demic, C.P., K.K. Chan, and J. Blum, Deep Trench Plasma-Etching of Single-Crystal Silicon Using Sf6/O2 Gas-Mixtures. Journal of Vacuum Science & Technology B, 1992. 10(3): p. 1105-1110.
- i. Yunkin, V.A., D. Fischer, and E. Voges, Highly Anisotropic Selective Reactive Ion Etching of Deep Trenches in Silicon. Microelectronic Engineering, 1994. 23(1-4): p. 373-376.
- j. Legtenberg, R., et al., Anisotropic Reactive Ion Etching of Silicon Using Sf6/O-2/Chf3 Gas Mixtures. Journal of the Electrochemical Society, 1995. 142(6): p. 2020-2028.
- k. Moss, S.J. and A. Ledwith, The chemistry of the semiconductor industry. 1987, Glasgow: Blackie. xiv, 426 p.
- l. Langan *et al.*, Method for plasma etching or cleaning with diluted NF.sub.3, US Patent 5413670, 1995.
- m. Wang, J.J., et al., High rate etching of SiC and SiCN in NF3 inductively coupled plasmas. Solid-State Electronics, 1998. 42(5): p. 743-747.
- n. Kim, B., et al., Use of a neural network to model SiC etching in a NF3 inductively coupled plasma. Modelling and Simulation in Materials Science and Engineering, 2005. 13(8): p. 1267-1277.

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:

- **Presentation in Gordon Research Conference(GRC), July 2012**
- **Invited talk to AVS International Symposium, October 2012**
- **Contributed talk at AVS International Symposium, October 2012**
  (N. Marchack, J. Chen and J. P. Chang, "Predictions of the Etch Behavior of Complex Oxide Films for High-k and Multiferroic Applications")
- **Contributed talk at AIChE Annual Meeting, October 2012**
  (N. Marchack, J. Chen and J. P. Chang, "Predictions of the Etch Behavior of Complex Oxide Films for High-k and Multiferroic Applications)

Publication:

- **Deliverable Report, P065582, "Non-PFC Plasma Chemistries for Patterning Complex Materials and Structures", January 2013**

Industrial Interactions and Technology Transfer

- **SRC Industrial Liaison, Satyarth Suri at Intel, April 2012**
- **ERC Webinar, June 2012**
- **Student presented research at AVS and AIChE meetings, 2012**
- **Conference call with Intel, September 2012 (Satyarth Suri, Bob Turkot)**
- **Conference call with Intel, November 30, 2012, (Satyarth Suri)**
- **Conference call with Intel, January 10, 2013, (Satyarth Suri)**
- **Conference call with Intel, February 21, 2013, (Satyarth Suri)**
- **Conference call with Intel, March 14, 2013, (Satyarth Suri)**

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

→ ***Complex oxides? Magnetic materials? Noble metals?***