Non-PFC Plasma Chemistries for Patterning Complex Materials/Structures

(*Task Number: 425.038*)

PIs:

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Graduate Students:

- **Jack Chen: PhD student, Chemical and Biomolecular Engineering, UCLA**
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Undergraduate Students:

- **(summer 2012)**

Other Researchers:

- **Hiroshi Yamamoto, Visiting Researcher, Electrical Engineering, Nagoya University**

Objectives

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

- **Formulate volatility diagrams for selected materials (Ni/Co/Fe) based on thermodynamic analysis**

- **Validate the theoretical assessment by performing etching experiments of these materials in Cl_2/BCl_3 chemistry using an ICP reactor with in-situ diagnostics (e.g. QMS, XPS)**

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**

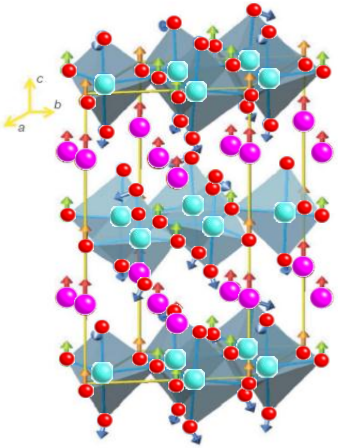
3. **Reduction in the use of chemicals by tailoring the chemistries to the specific materials to be removed**

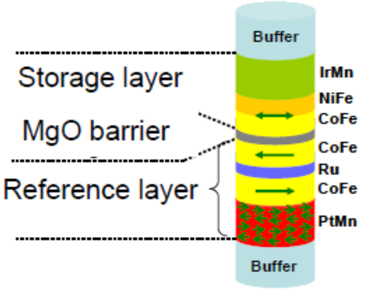
→ ***It is recognized that these are not yet quantitative, but as the project evolves, more quantitative measures will be provided***

Challenges and Method of Approach

Intrinsic Material Properties

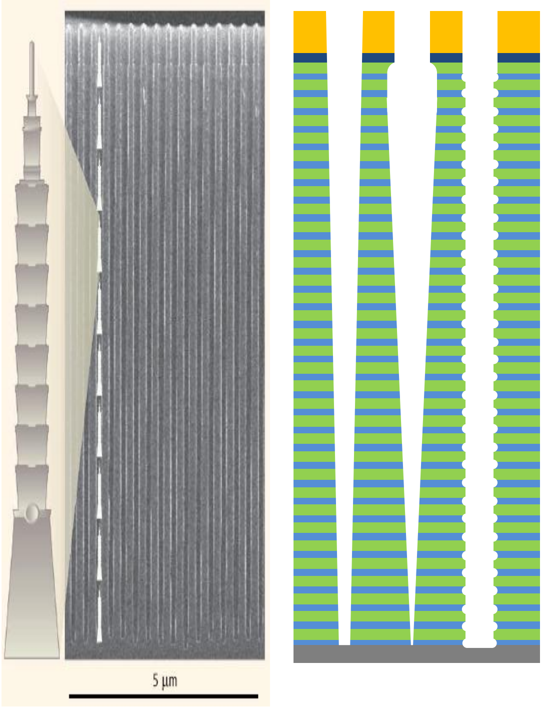
Less- or non-volatile etch products





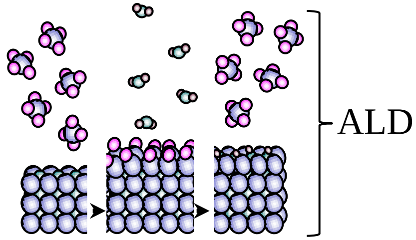
Structural Complexity

High aspect ratios, multiple layers



Atomic Scale Precision

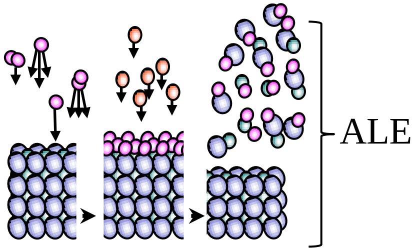
Atomic layer etch with no damage



Half Reactions for ALD of MO_2:

1)$M\text{-}(OH)_2(s)+MCl_4(g) \rightarrow M\text{-}O\text{-}M\text{-}Cl_2(s)+2HCl(g)$

2)$M\text{-}O\text{-}M\text{-}Cl_2(s)+2H_2O(g)\rightarrow M\text{-}O\text{-}M\text{-}(OH)_2(s)+2HCl(g)$



Half Reactions for ALE of M_xO_y:

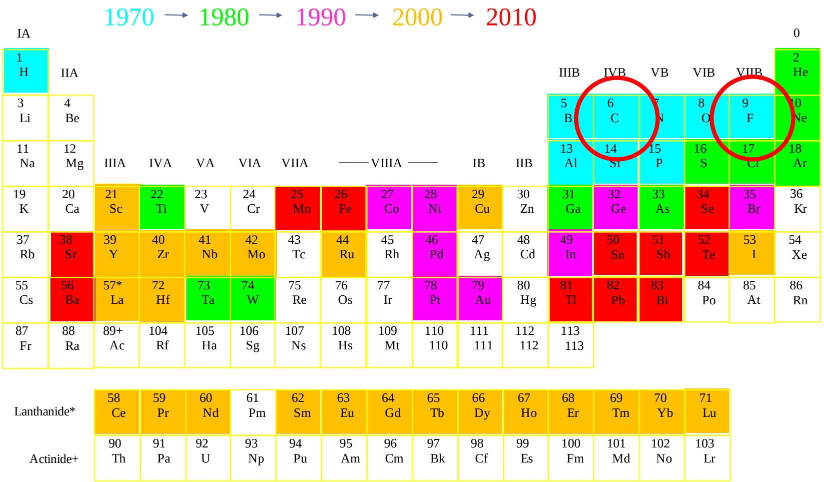
(1) $M_xO_y(s)+X^+(g)\rightarrow M_xO_y{}^*(s)$

(2) $M_xO_y{}^*(s)+ (cx+y)X(g)\rightarrow xMX_c(g)+yOX(g)$

- **Hard-to-etch materials, complex 3-D structures and atomic scale control pose major challenges to top-down patterning**

Approach for Etch-Resistant Materials

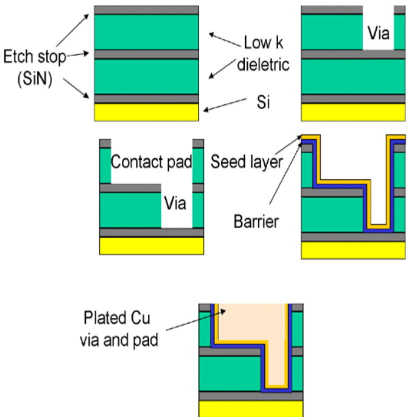
- Use more aggressive etch chemistries such as PFC
  - Fluorine is the most electro-negative element
  - Carbon reaction products (CO and CO_2) are volatile

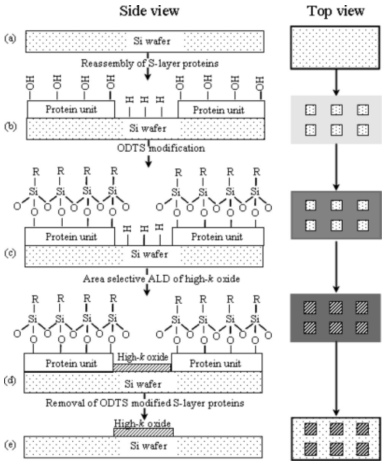


1970 → 1980 → 1990 → 2000 → 2010

IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA			IB	IIB	IIIB	IVB	VB	VIB	VIIB	0
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57* La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89+ Ac	104 Rf	105 Ha	106 Sg	107 Ns	108 Hs	109 Mt	110 110	111 111	112 112	113 113					

Lanthanide*	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinide+	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr





- Change processing approach to not etch these materials
  - Damascene process[1] for Cu
  - Area selective atomic layer deposition

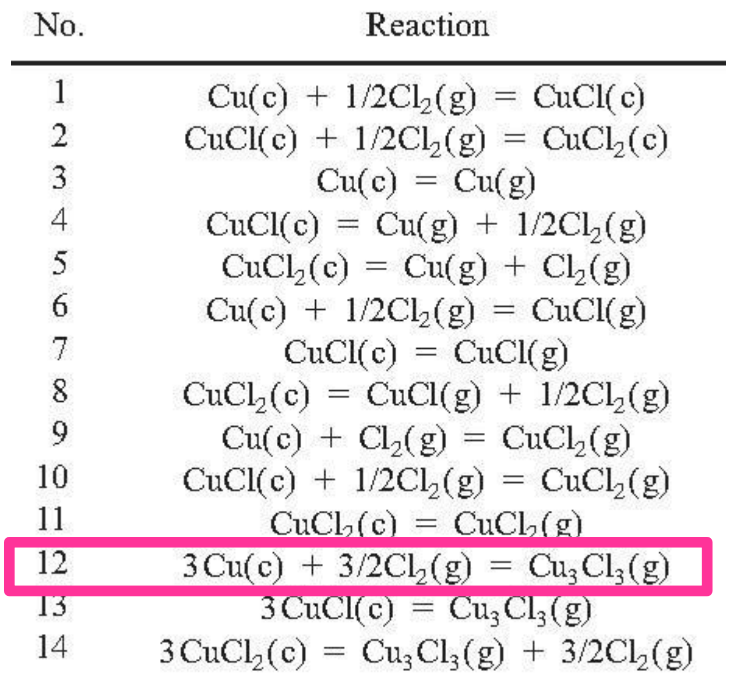
[1] P.C. Andricacos, C. Uzoh, J.O. Dukovic, J. Horkans, H. Deligianni, IBM, J. Res. Develop., Vol. 42, No.5(1998).

Systematic Approach - Thermodynamics

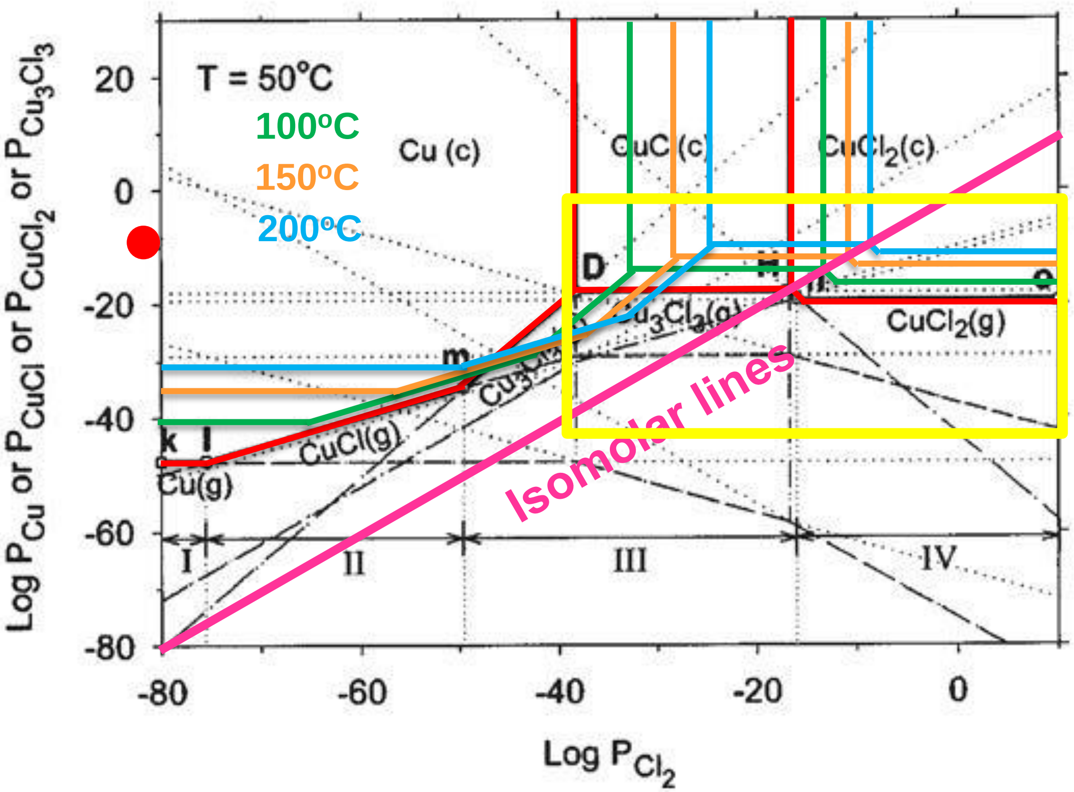
- **Thermodynamic approach can be systematic**
  - **If such data is available**
    - **NIST-JANAF Thermo-chemical tables**
    - **HSC Chemistry for windows, chemical reaction and equilibrium software with extensive thermo-chemical database**
    - **FACT, Facility for Analysis of Chemical Thermodynamics**
    - **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)



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	$3CuCl_2(c) = Cu_3Cl_3(g) + 3/2Cl_2(g)$

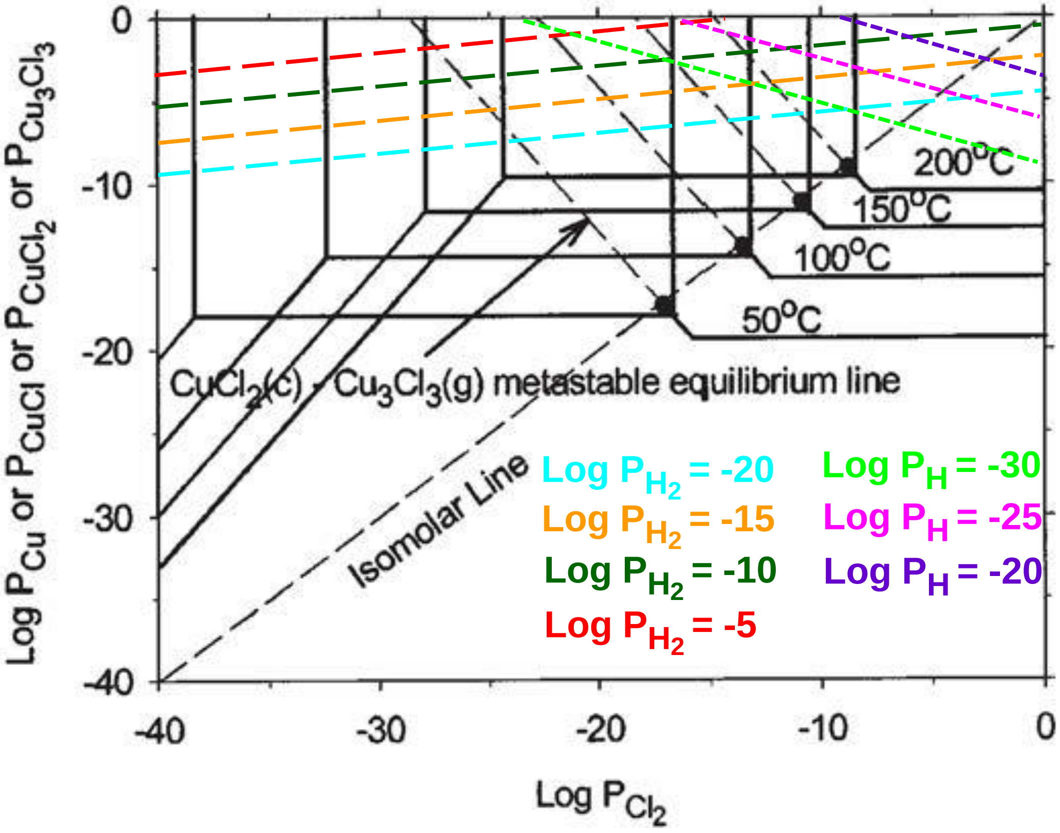


- **Target the volatile species**
- **Control pressure, temperature and gas composition**

N.S. Kulkarni, R.T. DeHoff, J. Electrochem. Soc., 149, G620 (2002).

A Case Study (Cu-Cl-H)

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	$CuCl(c) + 2H(g) = CuH(g) + HCl(g)$



Two step reaction (2002):

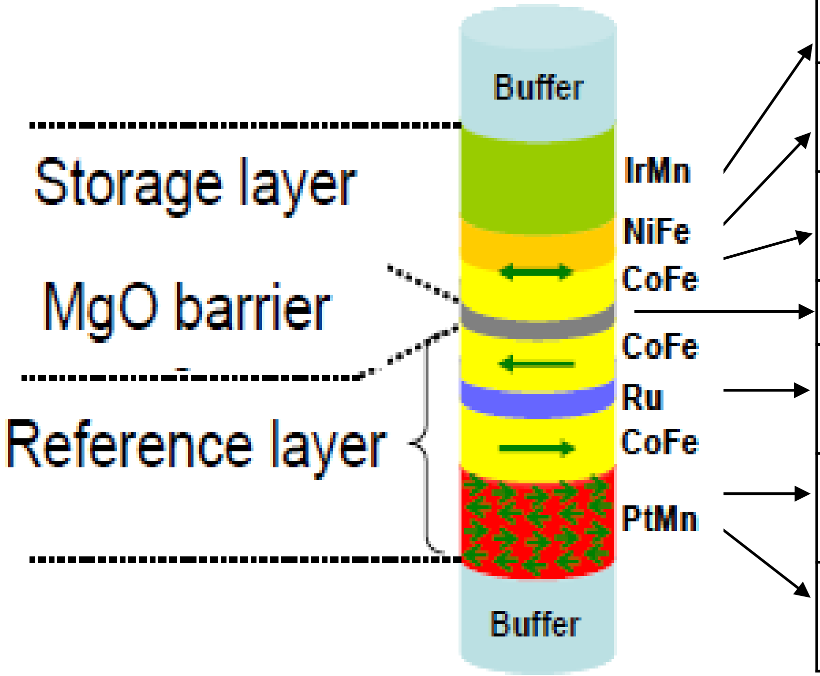
1) $Cu_{(c)} + 2Cl_{(g)}$
   → $CuCl_{2(c)}$ at low temp
2) $3 CuCl_{2(c)} + 3H_{(g)}$
   → $Cu_3Cl_{3(g)} + 3HCl_{(g)}$

Experimentally verified by Hess in 2007/2011

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

N.S. Kulkarni, R.T. DeHoff, J. Electrochem. Soc., 149, G620 (2002).

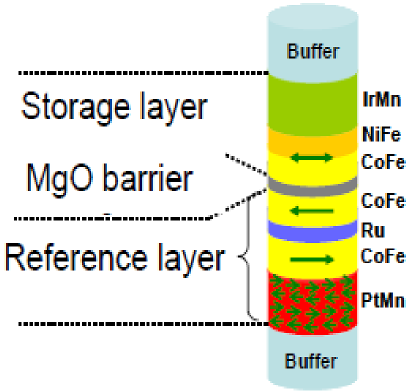
Potential Target Material Systems



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

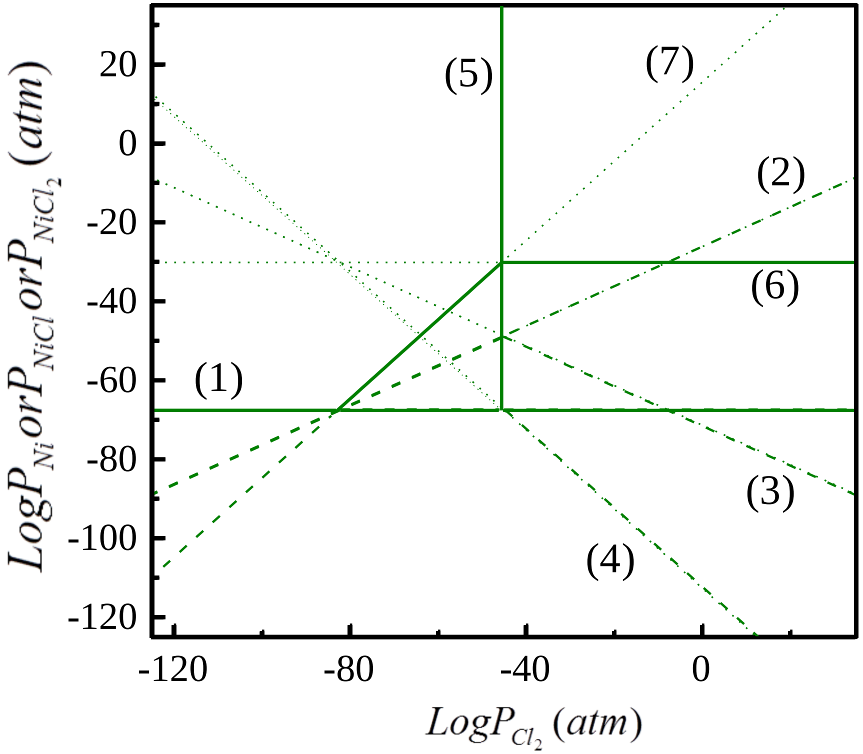
- **Problem of etch resistance compounded by need for selectivity in increasingly complex stacks, e.g. MTJs.**

General Thermodynamic Approach



		ΔH°	ΔG°	log(K)=-ΔG°/RT
1	$Ni(c) \rightarrow Ni(g)$	430.1	384.7	-67.4
2	$Ni(c) + 1/2Cl_2(g) \rightarrow NiCl(g)$	182.0	149.1	-26.1
3	$NiCl_2(c) \rightarrow NiCl(g) + 1/2Cl_2(g)$	486.9	407.8	-71.4
4	$NiCl_2(c) \rightarrow Ni(g) + Cl_2(g)$	735.0	643.5	-112.7
5	$Ni(c) + Cl_2(g) \rightarrow NiCl_2(c)$	-304.9	-258.8	45.3
6	$NiCl_2(c) \rightarrow NiCl_2(g)$	231.0	172.5	-30.2
7	$Ni(c) + Cl_2(g) \rightarrow NiCl_2(g)$	-73.9	-86.2	15.1

Volatility Diagram for Ni-Cl system at T=298.15K



Handbook of Chemistry and Physics, 85th ed., edited by D. R. Lide (CRC, Boca Raton, FL, 2004). NIST-JANAF Thermochemical Tables, 4th ed., M. W. Chase, Jr., Editor, American Chemical Society and the American Institute of Physics 1999.

- **Volatility diagram constructed for Ni system as test case**

Comparison of Fe/Co/Ni at 298K

1 $M(c) \rightarrow M(g)$

2 $M(c) + 1/2Cl_2(g) \rightarrow MCl(g)$

3 $MCl_2(c) \rightarrow MCl(g) + 1/2Cl_2(g)$

4 $MCl_2(c) \rightarrow M(g) + Cl_2(g)$

5 $M(c) + Cl_2(g) \rightarrow MCl_2(c)$

6 $MCl_2(c) \rightarrow MCl_2(g)$

7 $M(c) + Cl_2(g) \rightarrow MCl_2(g)$

8 $2M(c) + 2Cl_2(g) \rightarrow M_2Cl_4(g)$

9 $2MCl_2(c) \rightarrow M_2Cl_4(g)$

10 $M(c) + 3/2Cl_2(g) \rightarrow MCl_3(g)$

11 $MCl_2(c) + 1/2Cl_2(g) \rightarrow MCl_3(g)$

12 $MCl_2(c) + 1/2Cl_2(g) \rightarrow MCl_3(c)$

13 $MCl_3(c) \rightarrow MCl_3(g)$

14 $MCl_3(c) \rightarrow MCl(g) + Cl_2(g)$

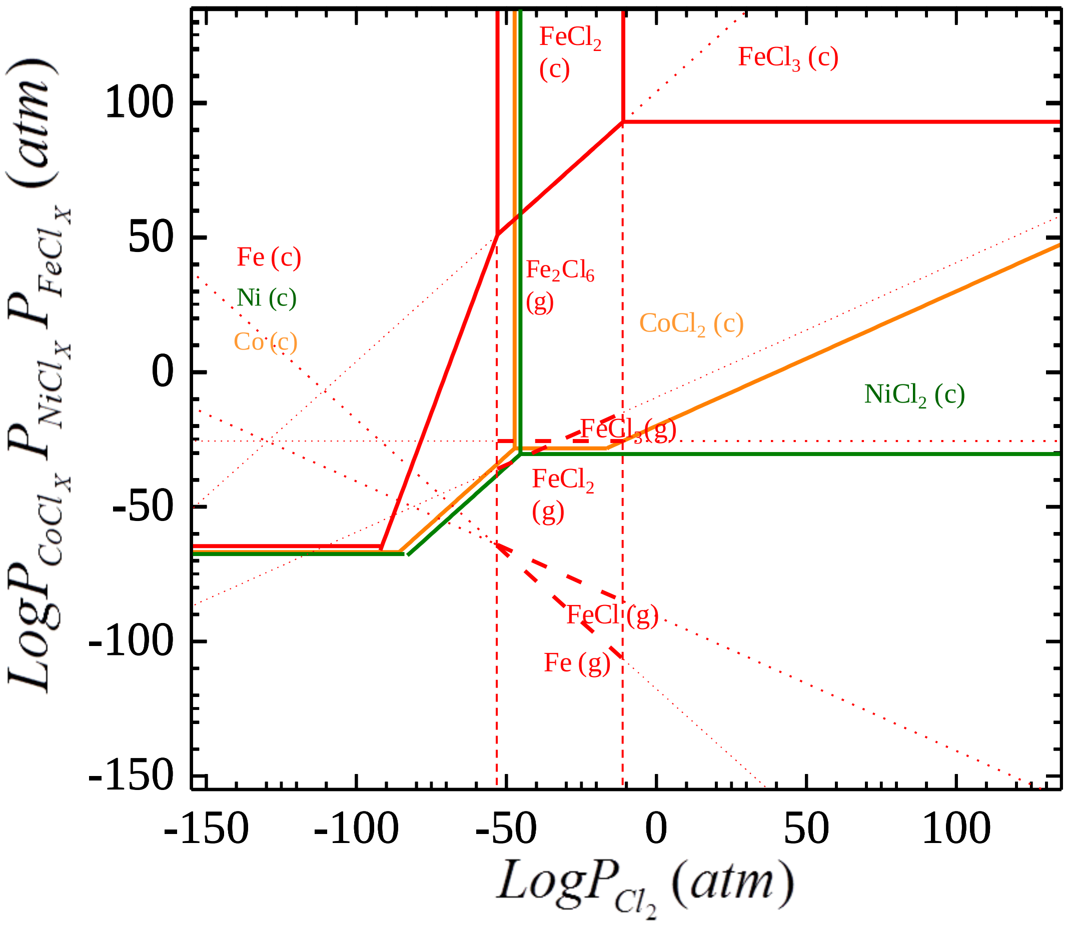
15 $MCl_3(c) \rightarrow MCl_2(g) + 1/2Cl_2(g)$

16 $MCl_3(c) \rightarrow M(g) + 3/2Cl_2(g)$

17 $2MCl_2(c) + Cl_2(g) \rightarrow M_2Cl_6(g)$

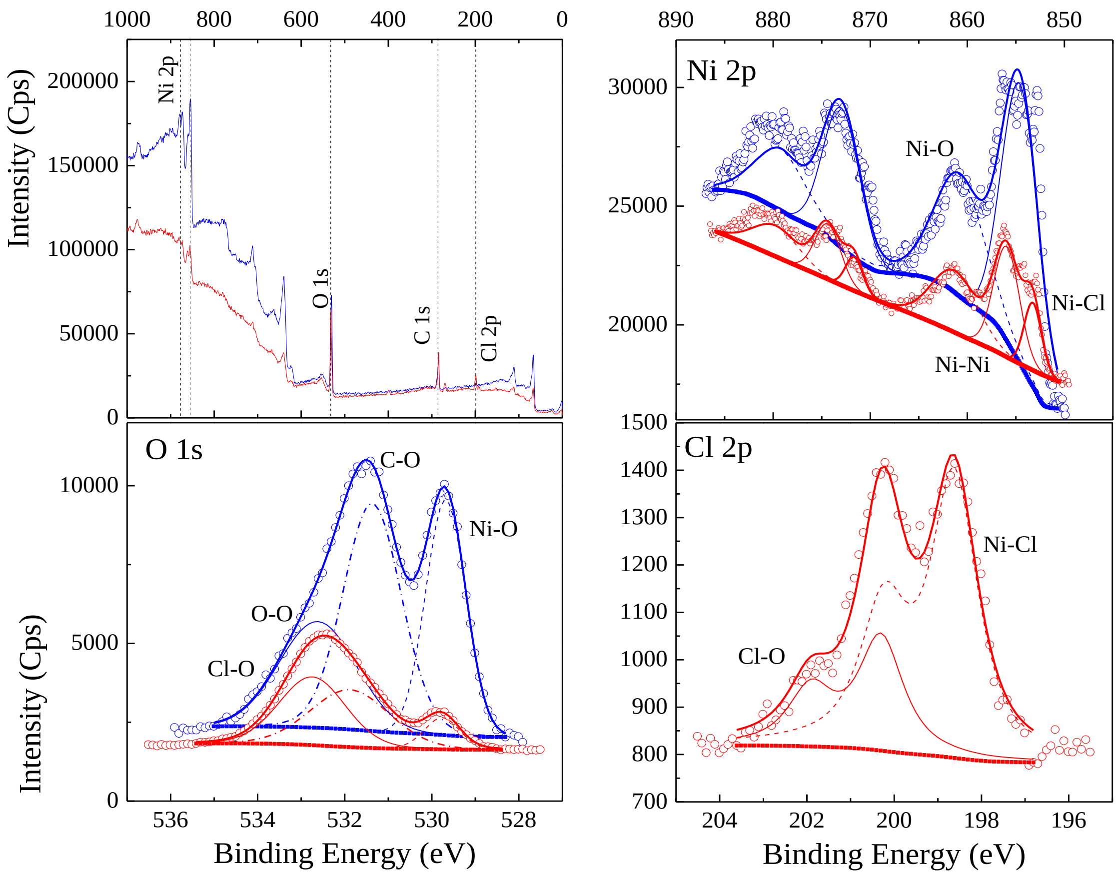
18 $2MCl_3(c) \rightarrow M_2Cl_6(g)$

19 $2M(c) + 3Cl_2(g) \rightarrow M_2Cl_6(g)$



- **Fe can be etched easier in Cl_2 than Ni or Co**

Etching of Ni in BCl_3



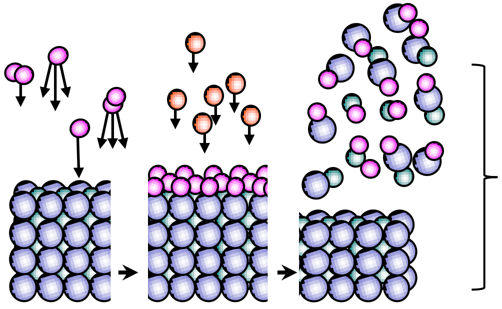
30 nm thick, sputter-deposited Ni film

BCl_3, 400W, 5mT, - 100V bias, 5 min

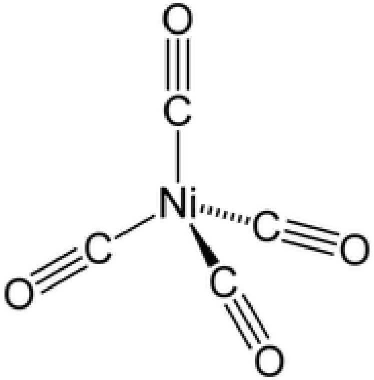
Element	Pre-etch	Post-BCl_3 etch
Ni	24%	10%
O	41%	39%
C	35%	43%
Cl	-	7%

- **Ni was etched in BCl_3 and Ni-Cl bonds were observed**

Non-Halogen Based Chemistries



Atomic Layer Etching



$Ni(CO)_4(g)$

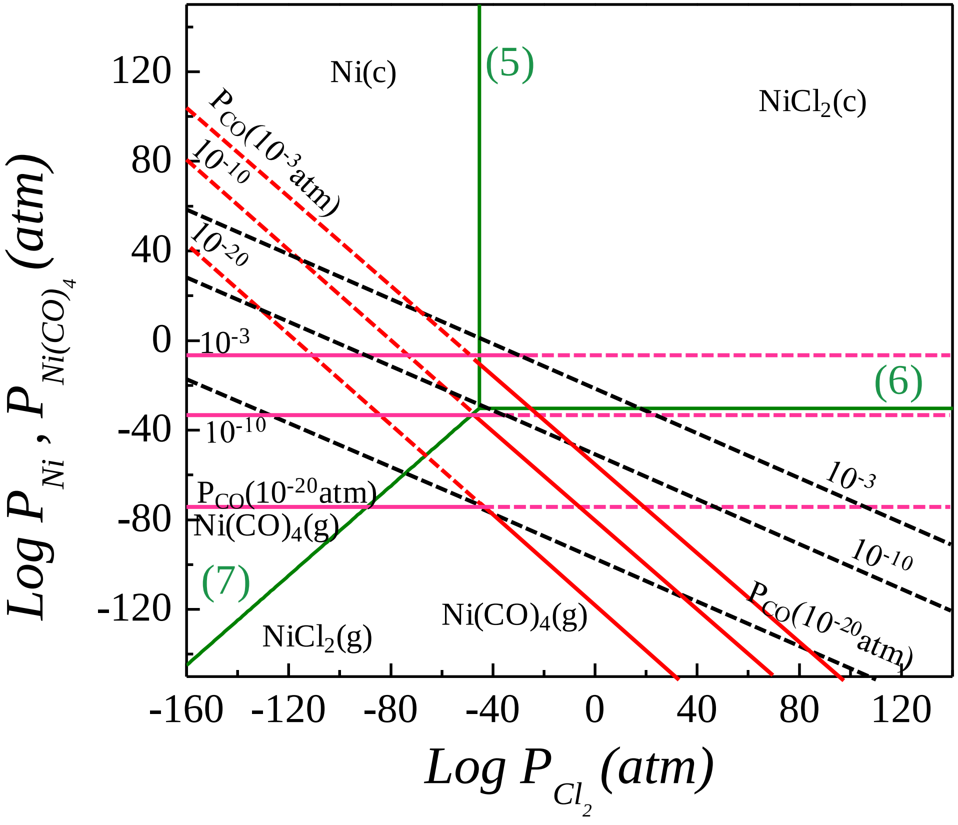
Product	MP	BP
$CoCl_2$	737	1049
$CoCO_3$	**280***	
$Co_2(CO)_8$	**51***	
$Co_4(CO)_{12}$	**60***	
$FeCl_3$	308	~316
$Fe(C_5H_5)_2$	172.5	249
$Fe(CO)_4H_2$	-70	-20*
$Fe(CO)_5$	**-20.5**	**103**
$Fe_2(CO)_9$	**100***	
$Fe_3(CO)_{12}$	**140**	
$NiCl_2$	1031	985 (subl)
NiF_2	**1474**	**1750**
$NiCl_2$	**1001**	
$NiBr_2$	**963**	
$Ni(CO)_4$	**-19**	**42(exp~60)**
$Ni(OH)_2$	**230**	
Ni_2O_3	**1990**	
$NiSO_4$	**100**	**840**

- **"Reverse engineering" of ALD points to organometallic chemistry as a viable alternative to halogens**

Etching of Ni by Cl_2 and CO

	ΔH°(kJ/mol)	ΔG°(kJ/mol)
$COCl_2(g)$	-219.1	-204.9
$NiCl_2(c)$	-305.3	-259
$Ni(CO)_4(g)$	-602	-587.2

	ΔG°	log(K)= -ΔG°/RT
(5) $Ni(c) + Cl_2(g) \rightarrow NiCl_2(c)$	**-258.8**	**45.3**
(6) $NiCl_2(c) \rightarrow NiCl_2(g)$	**172.5**	**-30.2**
(7) $Ni(c) + Cl_2(g) \rightarrow NiCl_2(g)$	**-86.2**	**15.1**
(8) $2NiCl_2(c) + 9CO(g) \rightarrow 2Ni(CO)_4(g) + COCl_2(g) + Cl_2(g)$	**126.2**	**-21.97**
(9) $NiCl_2(c) + 4CO(g) \rightarrow Ni(CO)_4(g) + Cl_2(g)$	**232.3**	**-40.4**
(10) $Ni(c) + 4CO(g) \rightarrow Ni(CO)_4(g)$	**-38.4**	**6.69**



- **Metastable lines show potential for increased removal of Ni through formation of $Ni(CO)_4$**

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**

→ ***Need to define a priority list of material systems to be studied by detailed thermodynamic analysis followed by kinetic measurements***

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

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

- **Invited talk to AVS International Symposium, October 2012**