Non-PFC Plasma Chemistries for Patterning Complex Materials/Structures

(*Task Number: 425.038)*

PIs:

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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**
- **Identify the non-PFC alternative for transition metal etching**

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**

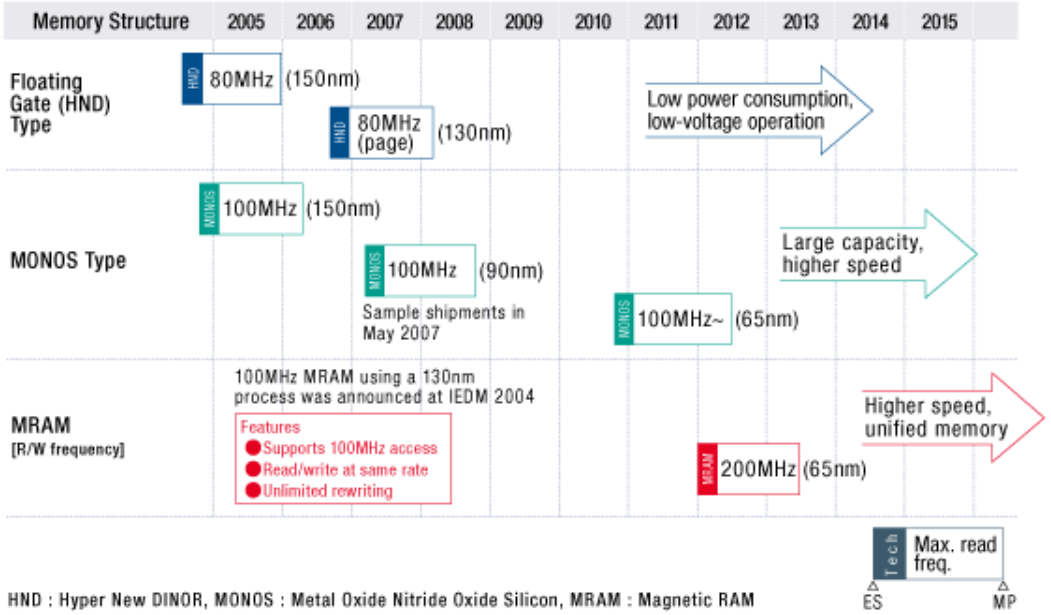
3. **Reduction in the use of chemicals by tailoring the chemistries to the specific materials to be removed**

Input from IAB

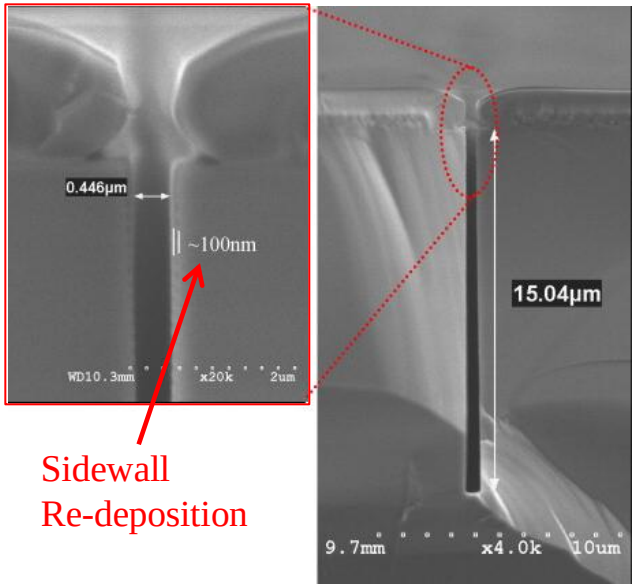
- **Focus on non-PFC materials**
- **Theoretical calculations must be paired with experimental data collection for validation**
- **Potential viability of NF3/O2 still needs to be validated – need an industry partners**
- **Support the need for industry partners to provide a platform for experimental validation**
- **Cost is a significant factor. Can any conclusions be drawn regarding how much NF_3 would have to be used relative to SF_6?**
- **Expand into new materials and carbon-doped oxide etch for greater impact**
- **N_2O is another area of interest (process fundamentals and abatement efficiency).**

Magnetic Devices Materials

Memory overview [RENASES]



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

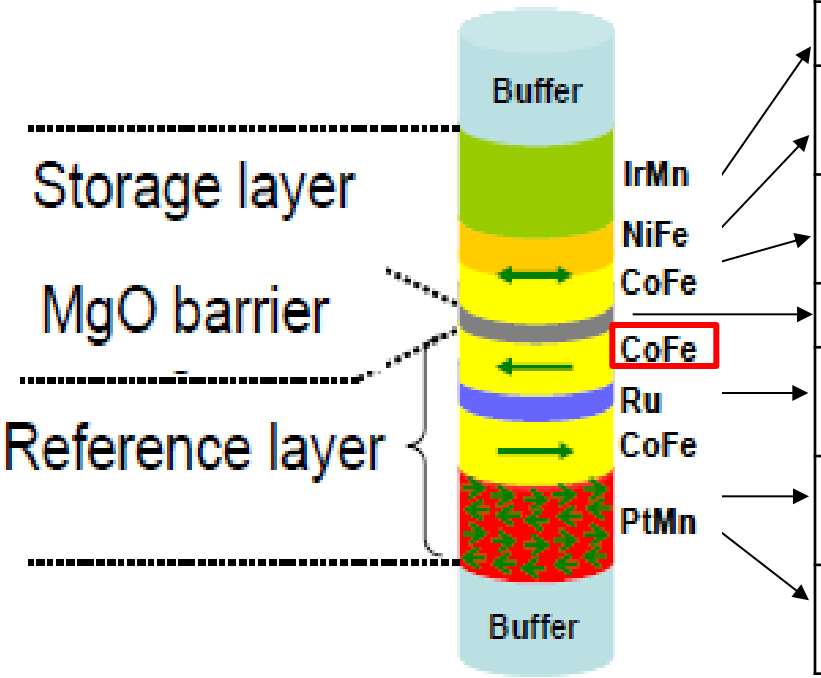


Sidewall Re-deposition

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

Availability of Thermodynamic Data

- **Some thermodynamic data is available for MCl_x and $M(CO)_x$ [1],[2].**

Metal	298K	ΔG°	$\Delta_f H^\circ$	ΔS°	MP(C)	BP(C)
		kJ·mol^{-1}	kJ·mol^{-1}	J·K^{-1} mol^{-1}		
Co-Cl_x	$CoCl(g)$	161.853	192.882	245.679		unstable
	$CoCl_2(c)$	-269.647	-312.545	109.266	735	1049
	$CoCl_2(g)$	-107.244	-93.722	298.500		
	$CoCl_3(g)$	-154.508	-163.594	334.209		
	Co2Cl4(g)	-333.955	-350.619	450.400		
Fe-Cl_x	FeCl(g)	173.720	251.076	257.855		
	FeCl2(c)	76.704	-341.158	118.534	677	
	FeCl2(g)	-230.238	-141.000	299.300		
	FeCl3(g)	-355.723	-253.100	344.200		
	Fe2Cl4(g)	-569.880	-431.400	484.399		
Ni-Clx	NiCl(g)	106.896	182.000	251.900		
	NiCl2(c)	-334.446	-305.332	97.650	1031	
	NiCl2(g)	-161.754	-73.990	294.364		
Co-(CO)x	$Co(CO)_3$				280	
	$Co_2(CO)_8$				51	
	$Co_4(CO)_{12}$				60	
Fe-(CO)x	$Fe(CO)_5$				-20.5	103
	$Fe_2(CO)_9$				100	
	$Fe_3(CO)_{12}$				140	
Ni-(CO)x	$Ni(CO)_4$				-19	42

- **For unavailable thermodynamic data, it needs to be calculated by DFT or MD.**

[1] HSC chemistry for windows, ver. 7 [2] NIST-JANAF Thermochemical Tables

Volatility Diagram for Co-Cl System

Step 1. Proposed reaction list for Co-Cl system

Equilibrium between condensed phases	
1	$Co(c) + 1/2Cl_2(g) \leftrightarrow CoCl(c)$
2	$CoCl(c) + 1/2Cl2(g) \leftrightarrow CoCl_2(c)$
Equilibrium between Co(g) and condensed phases	
3	$Co(c) \leftrightarrow Co(g)$
4	$CoCl(c) \leftrightarrow Co(g) + 1/2Cl_2(g)$
5	$CoCl_2(c) \leftrightarrow Co(g) + Cl_2(g)$
Equilibrium between CoCl(g) and condensed phases	
6	$Co(c) +1/2Cl_2(g) \leftrightarrow CoCl(g)$
7	$CoCl(c) \leftrightarrow CoCl(g)$
8	$CoCl_2(c) \leftrightarrow CoCl(g) +1/2Cl_2(g)$
Equilibrium between $CoCl_2(g)$ and condensed phases	
9	$Co(c)+ Cl_2(g) \leftrightarrow CoCl_2(g)$
10	$CoCl(c)+ 1/2Cl_2(g) \leftrightarrow CoCl_2 (g)$
11	$CoCl_2(c) \leftrightarrow CoCl_2(g)$

- **The list of relevant reactions for constructing the volatility diagram for the Co-Cl system is given in the table.**

Volatility Diagram for Co-Cl System

Step 2. Calculating equilibrium constant of the reactions

	G at 400K [1],[2] (kJ/mol)
$Cl_2(g)$	-89.7
$H_2(g)$	-52.7
H(g)	171.7
Co(g)	352.5
Co(c)	-12.4
CoCl(c)	-204.7
CoCl(g)	93.4
$CoCl_2(c)$	-357.4
$CoCl_2(g)$	-213.8
$Co_2Cl_4(g)$	-532.6

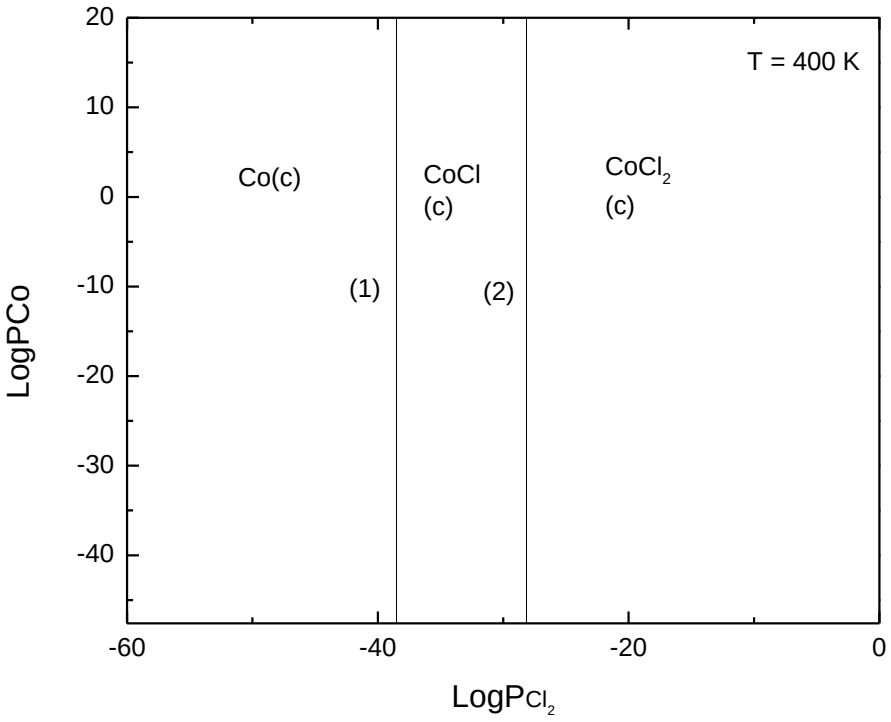
	Reaction	ΔG (kJ/mol)	Log K
1	$Co(c) + 1/2Cl_2(g) \rightarrow CoCl(c)$	-147.4	19.2
2	$CoCl(c) + 1/2Cl_2(g) \rightarrow CoCl_2(c)$	-107.7	14.0
3	$Co(c) \rightarrow Co(g)$	364.9	-47.6
4	$CoCl(c) \rightarrow Co(g) + 1/2Cl_2(g)$	512.4	-66.9
5	$CoCl_2(c) \rightarrow Co(g) + Cl_2(g)$	620.2	-80.9
6	$Co(c) +1/2Cl_2(g) \rightarrow CoCl(g)$	150.7	-19.6
7	$CoCl(c) \rightarrow CoCl(g)$	298.2	-38.9
8	$CoCl_2(c) \rightarrow CoCl(g) +1/2Cl_2(g)$	406.0	-53.0
9	$Co(c)+ Cl_2(g) \rightarrow CoCl_2(g)$	-111.6	14.5
10	$CoCl(c)+ 1/2Cl_2(g) \rightarrow CoCl_2 (g)$	35.7	-4.6
11	$CoCl_2(c) \rightarrow CoCl_2(g)$	143.5	-18.7

- **Thermodynamic parameters are referred to HSC[1] and JANAF[2] data base.**
- **ΔG can be calculated from the Gibbs free energy of each molecule and the stoichiometry of a reaction. Equilibrium constant can be obtained from ΔG.**

[1] HSC chemistry for windows, ver. 7 [2] NIST-JANAF Thermochemical Tables

Volatility Diagram for Co-Cl System

Step 3. Equilibrium between condensed phases



	Reaction	ΔG (kJ/mol)	log K
1	$Co(c) + 1/2Cl_2(g) \rightarrow CoCl(c)$	-147.4	19.2
2	$CoCl(c) + 1/2Cl_2(g) \rightarrow CoCl_2(c)$	-107.7	14.0

In reaction 1

$$\log K = \log \frac{a(CoCl(c))}{a(Co(c)) \times P(Cl_2(g))^{1/2}}$$

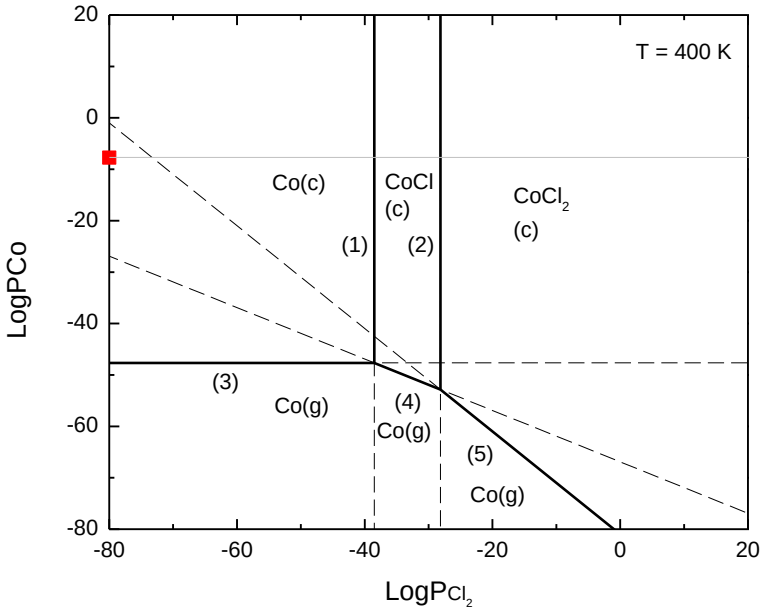
$$\log P(Cl_2(g)) = -2 \times \log K = -38.4$$

assuming, $a(CoCl(c)) = a(Co(c)) = 1$

- Cl_2 pressure at the equilibrium state can be calculated from the equilibrium constant.
- As $Cl_2(g)$ partial pressure increases, chlorination is observed, but still $CoCl_2$ exist as condensed phase.

Volatility Diagram for Co-Cl System

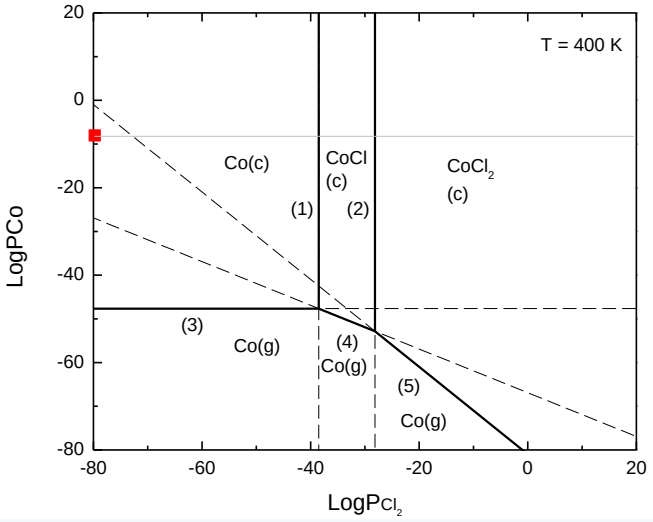
Step 4. Equilibrium between Co(g) and condensed phases



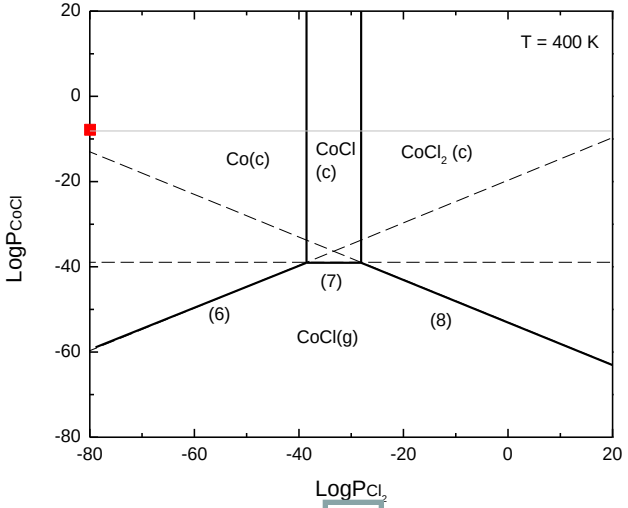
	Reaction	ΔG (kJ/mol)	Log K
1	$Co(c) + 1/2Cl_2(g) \rightarrow CoCl(c)$	-147.4	19.2
2	$CoCl(c) + 1/2Cl_2(g) \rightarrow CoCl_2(c)$	-107.7	14.0
3	$Co(c) \rightarrow Co(g)$	364.9	-47.6
4	$CoCl(c) \rightarrow Co(g) + 1/2Cl_2(g)$	512.4	-66.9
5	$CoCl_2(c) \rightarrow Co(g) + Cl_2(g)$	620.2	-80.9

Volatility Diagram for Co-Cl System

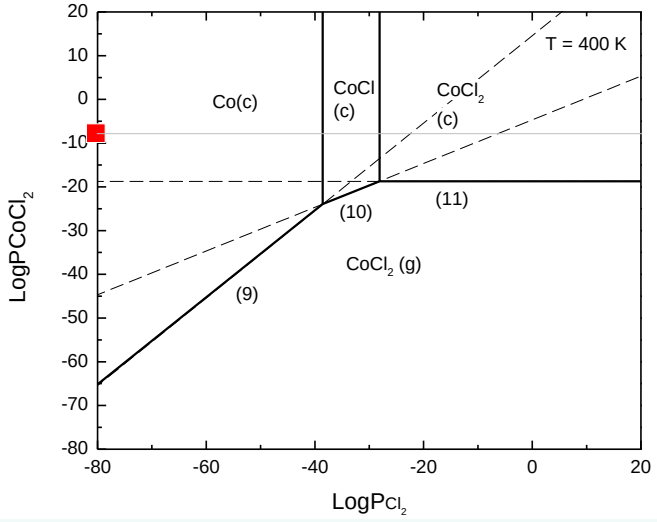
Co(g) and condensed phases



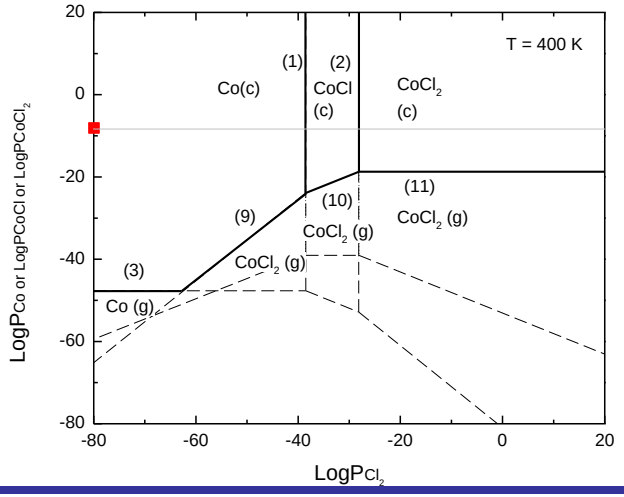
CoCl(g) and condensed phases



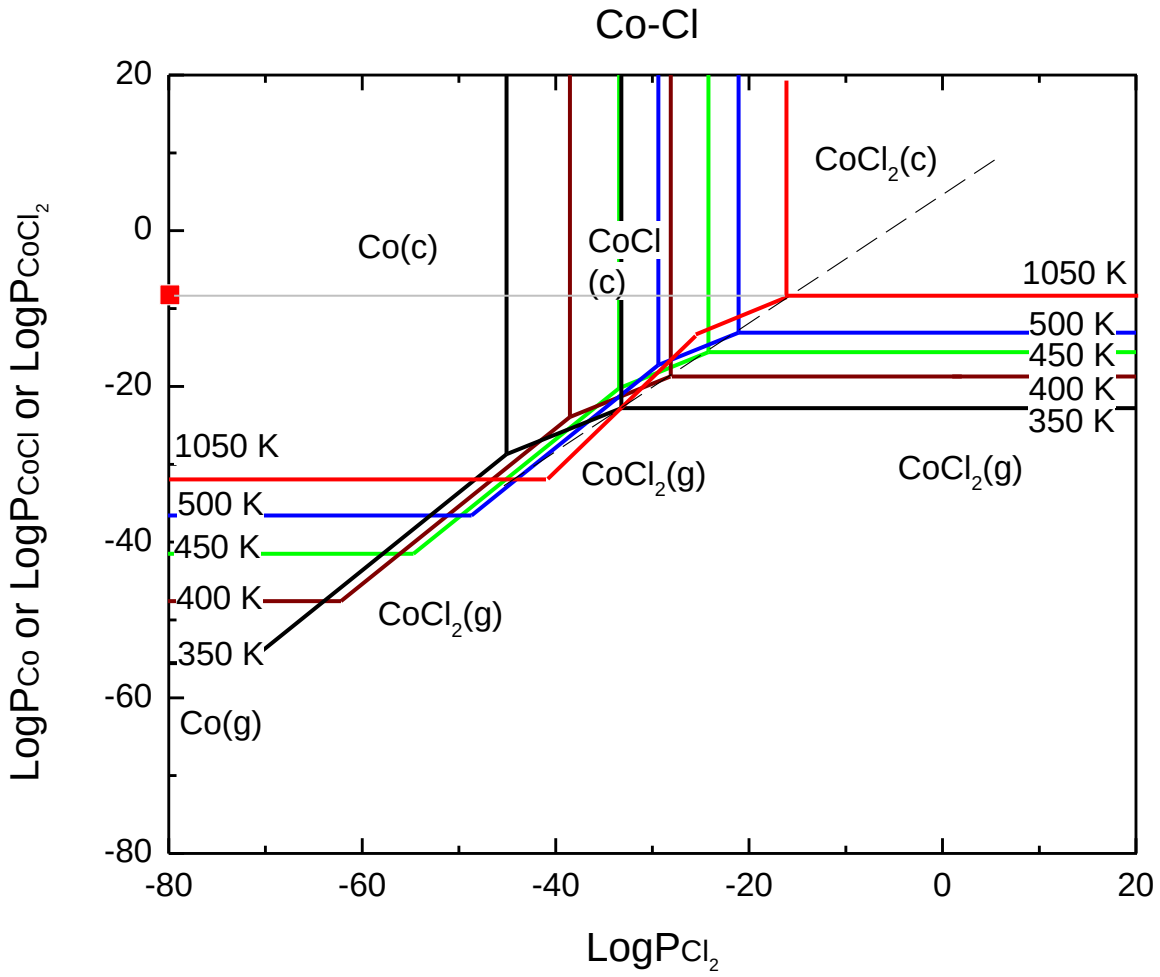
$CoCl_2$(g) and condensed phases



Combined phase diagram

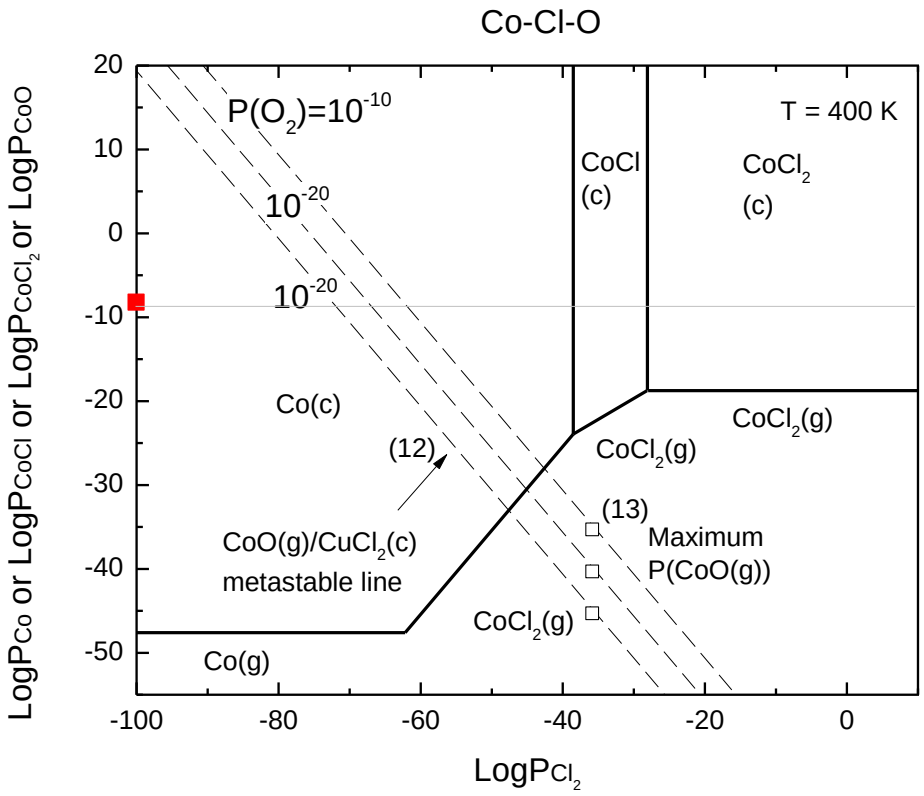


Effect of Temperature



- **$CoCl_2$ becomes volatile at 1050 K.**

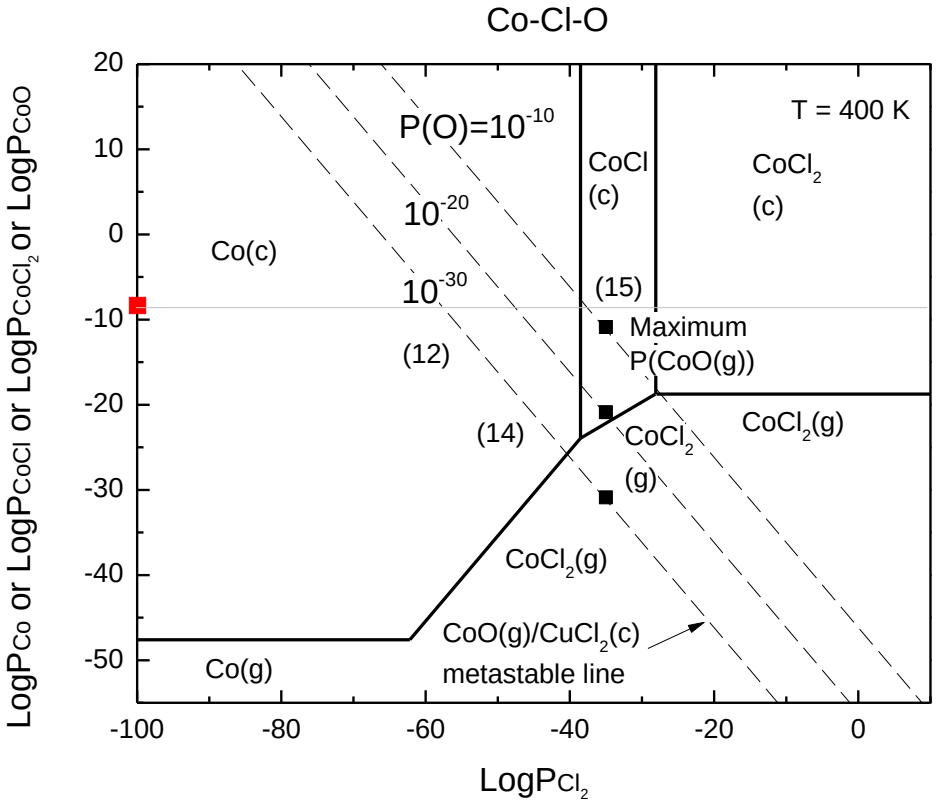
Effect of Molecular Oxygen



	Reaction	ΔG (kJ/mol)	logK
12	$CoCl_2(c)+ 1/2O_2(g) \rightarrow CoO(g)+Cl_2(g)$	502.6	-65.6
13	$CoCl_2(c) + 2/3O_2(g) \rightarrow CoO(g)+2OCl(g)$	697.3	-91.0

- **O_2 addition does not improve the vapor pressure of etch product.**

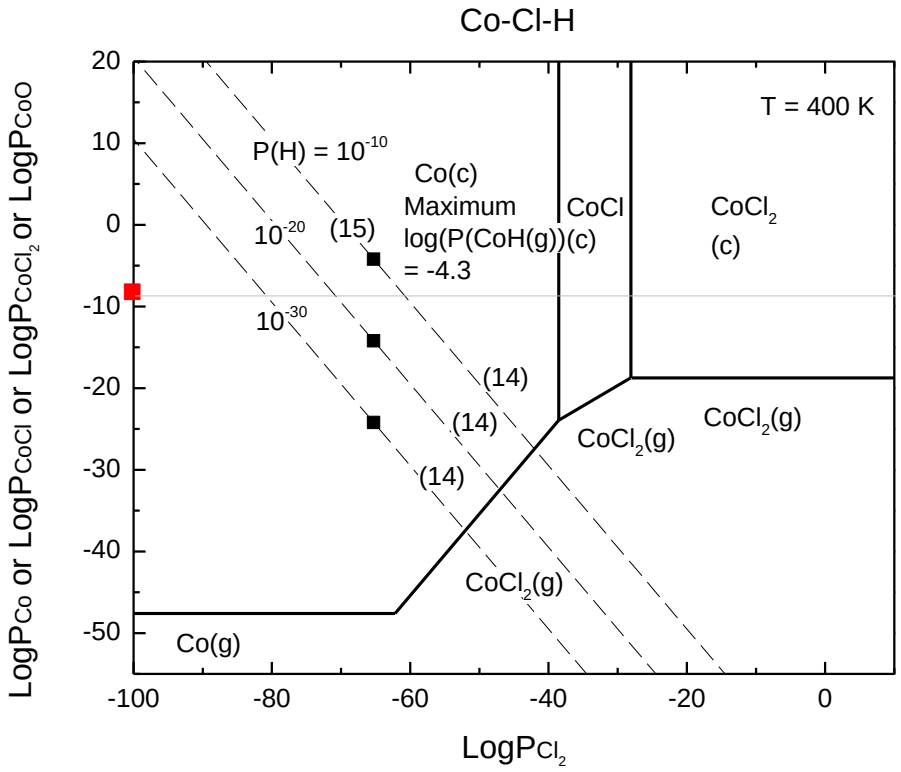
Effect of Atomic Oxygen



	Reaction	ΔG (kJ/mol)	logK
14	$CoCl_2(c)+ O(g) \rightarrow CoO(g)+Cl_2(g)$	277.0	-36.2
15	$CoCl_2(c) + 3O(g) \rightarrow CoO(g)+2OCl(g)$	20.0	-2.6

- **O radical addition showed the vapor pressure enhancement.**

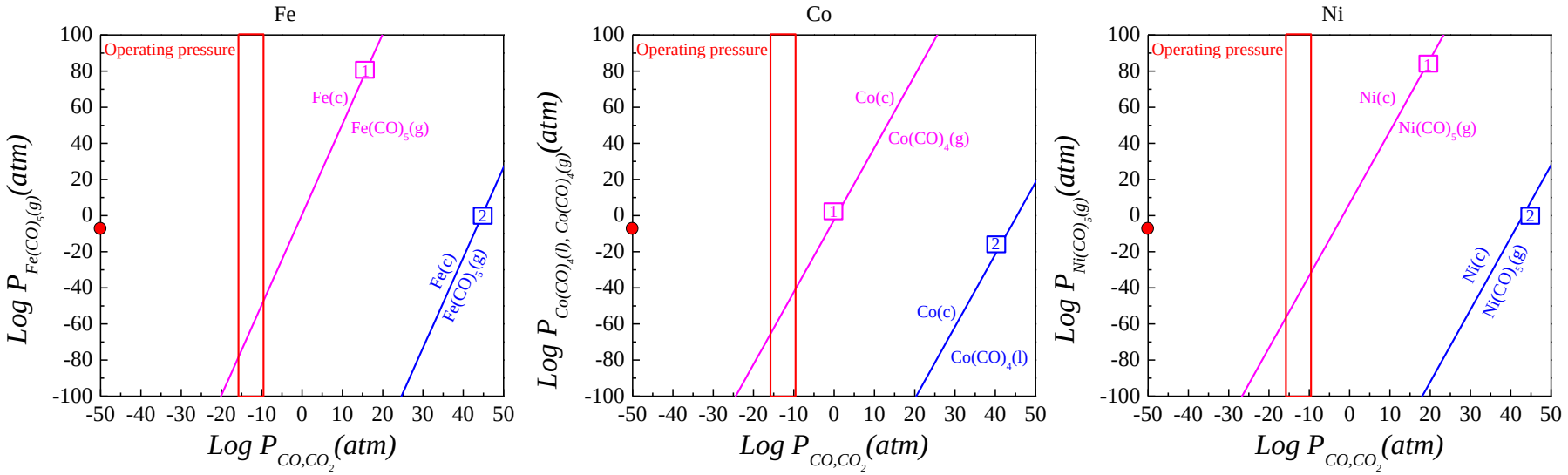
Effect of Atomic Hydrogen



	Reaction	ΔG(Kj/mol)	logK
14	$CoCl_2(c) + H(g) \rightarrow CoH(g)+Cl_2(g)$	455.6	-59.6
15	$CoCl_2(c) + 3H(g) \rightarrow CoH(g)+2HCl(g)$	-133.2	17.4

- **Atomic hydrogen addition can produce the volatile etch product.**

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			

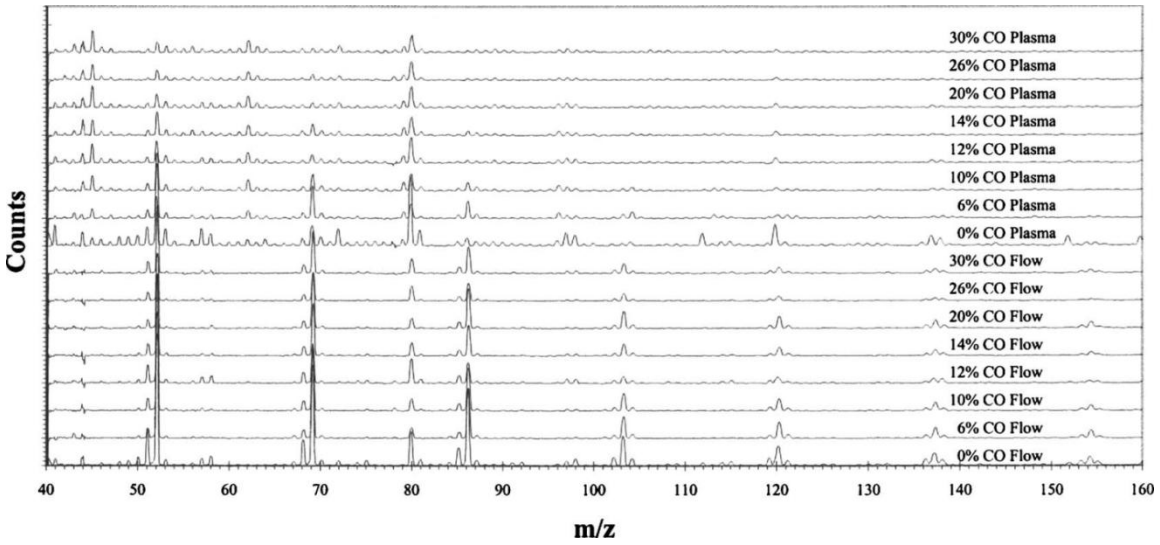
- Volatility of M-$(CO)_x$ complexes: $Ni(CO)_5$>$Fe(CO)_5$>$Co(CO)_4$

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

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.

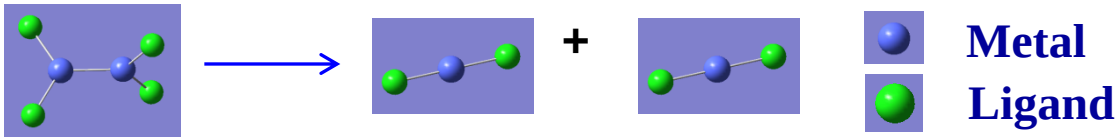
[1] A. Orland, J. Vac. Sci. Technol. B 23, 2005

The need for Thermodynamic Data

- **If the thermodynamic data is not available, (ex. MCH_3NO)**

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(>5), so MD calculation will be tested to get an accurate value

MD calculation

- System for simulation :

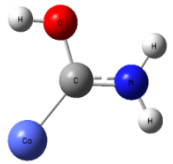
  ML_2, ML_3 (M=Co, Ni, Fe), L: organic ligand. (a system comprised of 125 metal atoms)
- Simulation program : DLPOLY
- ΔH_{vap} could be calculated

$\Delta_f H$ of M-CH_3NO Complexes

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

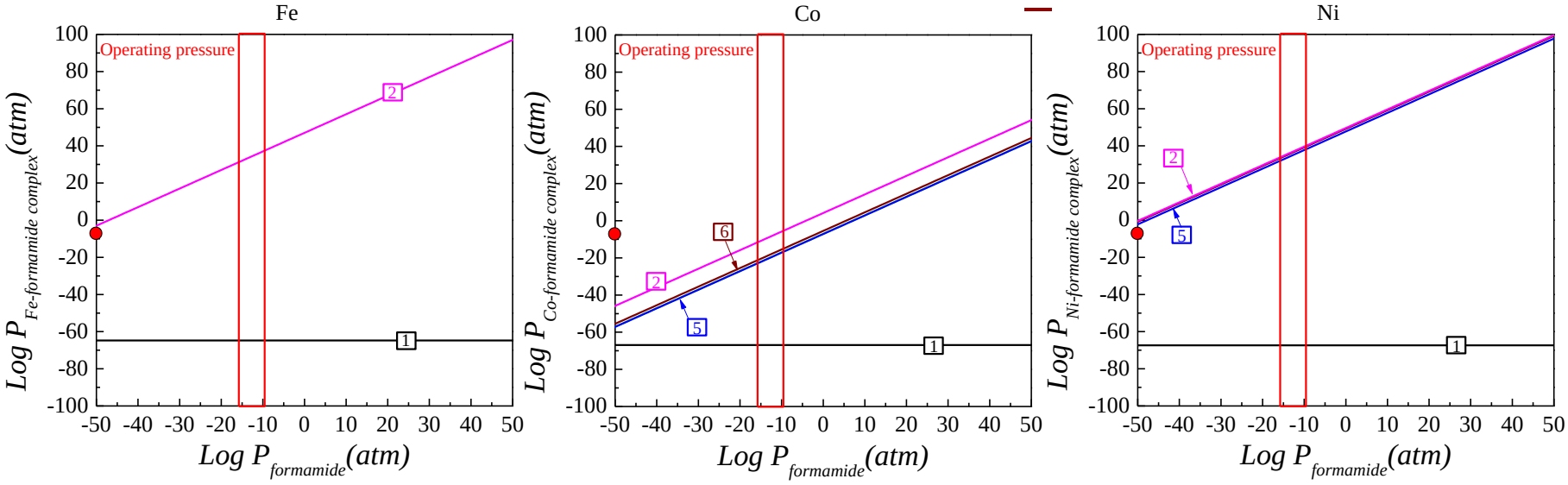
$\Delta_f H$(kJ/mol)	[MCH_3NO]	[MCH_3NO]	[MCH_3NO]	[MCH_3NO]
Fe	-76.2	x	x	x
Co	x	240.4	240.8	228.7
Ni	-76.8	x	-71.4	-77.9
x=unstable product				



- 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

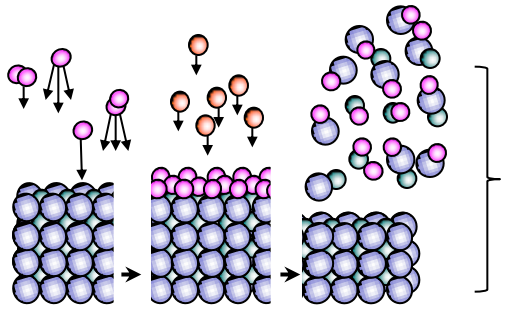


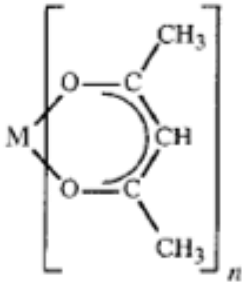
	Reation_ΔG(kJ/mol)	Fe	Co	Ni
1	**M**(c) → **M**(g)	369.8	382.1	384.7
2	CH_3NO(g) +**M**(g)→ 	-268.4	-23.7	-283.3
4	CH_3NO(g) +**M**(g)→ 	x	56.3	x
5	CH_3NO(g) +**M**(g)→ 	x	40.4	-272.5
6	CH_3NO(g) +**M**(g)→ 	x	40.9	-280.6

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

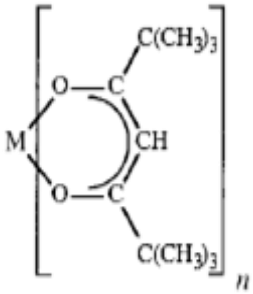
NIST-JANAF Thermo-chemical tables, 2012

Organometallic Chemistry





Acetylacetonate (ACAC)



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

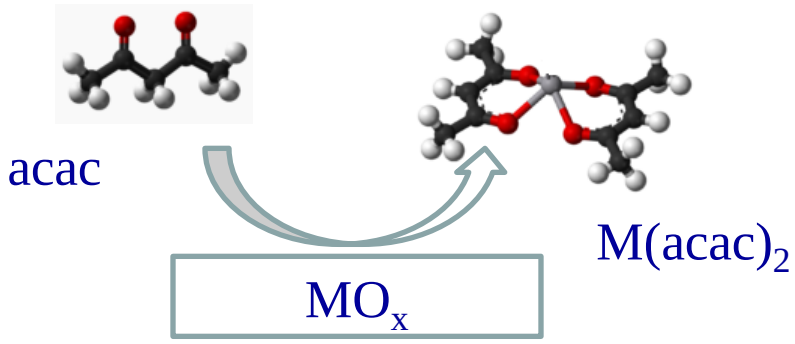
Product	MP	BP
$CoCl_2$	737	1049
$CoCO_3$	**280***	
$Co_2(CO)_8$	**51***	
$Co_4(CO)_{12}$	**60***	
$Co(acac)_2$	170	181 (exp~200)
$Co(acac)_3$	211	170 (exp~190)
$Co(tmhd)_2$	254	171 (exp~192)
$Co(tmhd)_3$	143	161 (exp~179)
$FeCl_3$	308	~316
$Fe(C_5H_5)_2$	172.5	249
$Fe(CO)_4H_2$	-70	-20*
$Fe(CO)_5$	**-20.5**	**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

Organometallic Chemistry

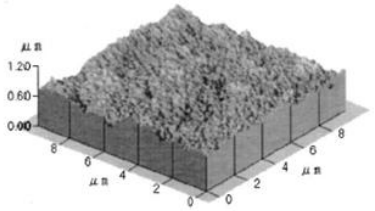
$M(acac)_n$ vaporization induced by acac exposure



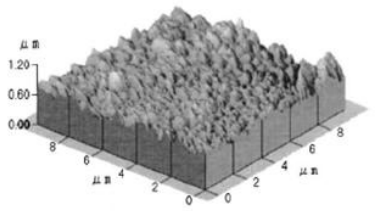
M : Fe[1], Ni[2], Cu[3]

[1] Cu etch with hfac vapor at 200 °C

Surface morphology change



Before Hfac vapor etching
RMS roughness : 50 nm



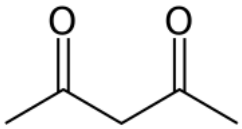
After Hfac vapor etching
RMS roughness : 90 nm

- It is reported that acac (acetylacetone) or hfac (hexafluoro acetylacetone) can etch Fe, Ni, and Cu films.
- For copper, hfac caused the morphology change and a reasonable etch rate.

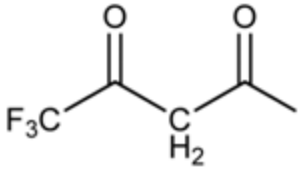
[1] S.W. Kang et al. JVST B. 17 (1999) 154

Organometallic Chemistry to Etch Ni

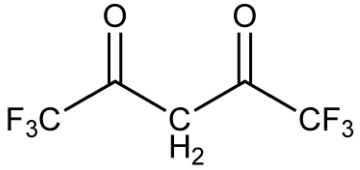
Acac (acetylacetone)



Tfac (trifluoro acetylacetone)

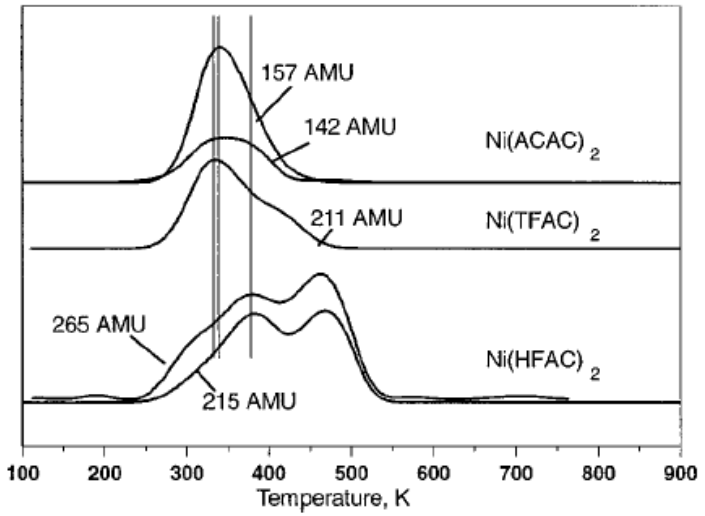


Hfac (hexafluoro acetylacetone)



[2] $Ni(acac)_2$, $Ni(tfac)_2$, and $Ni(hfac)_2$

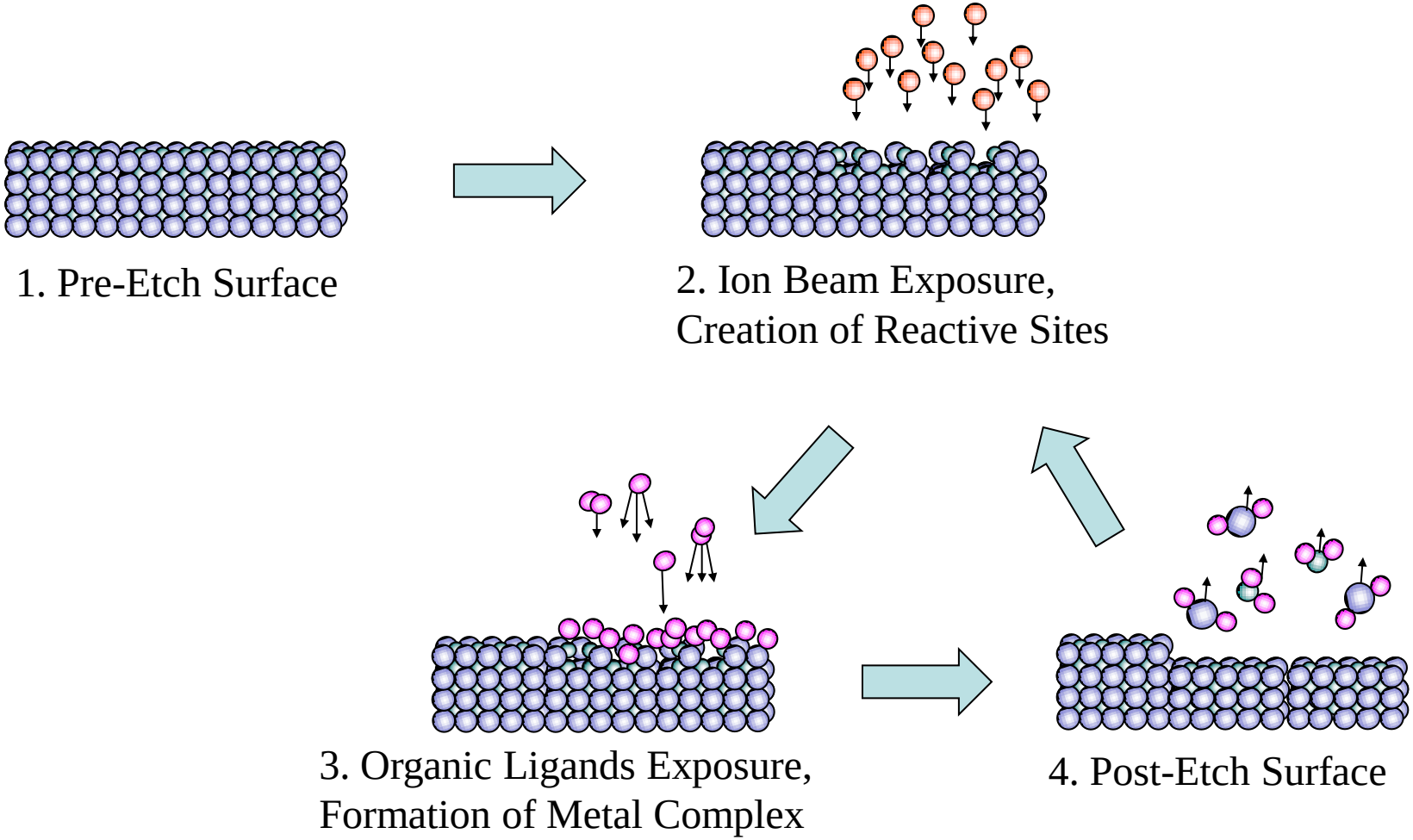
- Thermal desorption spectroscopy using mass spectrometer



- Mass spectroscopy data showed that acac, tfac, and hfac dose generate $Ni(acac)_2$, $Ni(tfac)_2$, and $Ni(hfac)_2$, respectively.

[2] R. I. Masel et al. JVST A. 16 (1998) 3259

Ion Beam Assisted Chemical Etching



- Ion beam generate active sites
- Organic molecules react with active sites and generate volatile etch products.

Summary

- The volatility diagram is a useful tool to calculate the vapor pressure of the etch product.
- $CoCl_2$, $NiCl_2$, and $FeCl_2$ are not volatile enough and needs secondary etchant to enhance the vapor pressure of etch product.
- Hydrogen radical addition improve the vapor pressure of the etch product.
- Some of the complex products are stable which implies the potential etch product in CO/NH_3 plasma treatment.
- Acac, tfac, and hfac are used to chemically etch for metal films.
- Ion beam assisted chemical vapor etch can generate the active site to make a metal atom react with organic ligand.

Reference

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Future Plans

Next Year Plans

- 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 etch product from plasma processes
- Propose the plasma chemistries via thermodynamic calculation

Publications, Presentations, and Recognitions/Awards

Presentation:

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

Publication:

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

Industrial Interactions and Technology Transfer

- **Conference call with Intel, September 2012 (Satyarth Suri, Bob Turkot)**
- **Conference call with Intel, 30, November, 2012 (Satyarth Suri)**
- **Conference call with Intel, 10, January, 2013 (Satyarth Suri)**
- **Conference call with Intel, 21, February, 2013 (Satyarth Suri)**
- **Visit Intel, Portland, OR, 3, April, 2013, (Bob Turkot, Satyarth Suri)**
- **Conference call with SRC, 24, April, 2013 (Bob Haveman)**