Alternative Etchants for Magnetic Materials

(*Task Number: 425.046*)

PIs:

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Graduate Students:

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

Other Researchers:

- **Taeseung Kim, Postdoc, Chemical and Biomolecular Engineering, UCLA**

Objectives

- Assess the feasibility of chemistries in patterning magnetic materials in MRAM cell
- Identify alternative chemistry for magnetic metal etch
- Screen the candidates of chemistries by comparing the pressure of primary etch product in the volatility diagram
- Verify the thermodynamic calculation by performing the plasma etching experiments

ESH Metrics and Impact

1. **Reduction in the use of PFC gases by focusing on alternative chemistries in the etch of magnetic materials**

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

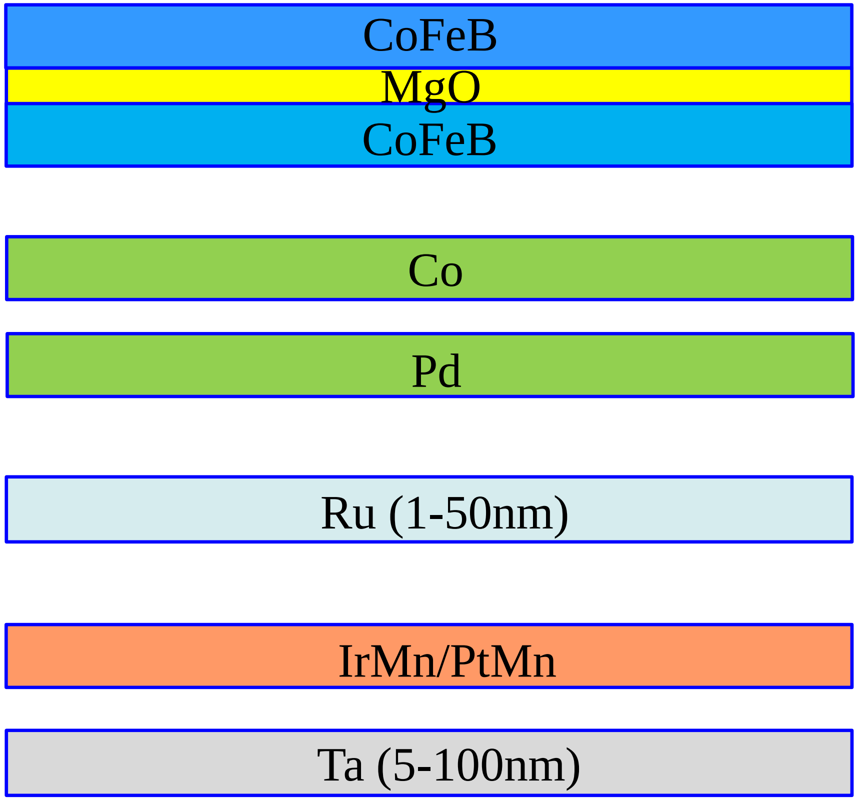
3. **The thermodynamic calculation of metal etch has been verified experimentally**

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

Target of MRAM Metal Etch

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

Intel specified metrics:


CoFeB

MgO

CoFeB

Co

Pd

Ru (1-50nm)

IrMn/PtMn

Ta (5-100nm)

Focus on:

1	Carbonyl formation using CO/NH_3 and methanol chemistries
2	Are the carbonyl thermodynamically favored? →Volatility analysis
3	Other potential chemistries to etch metals

Priority of research:

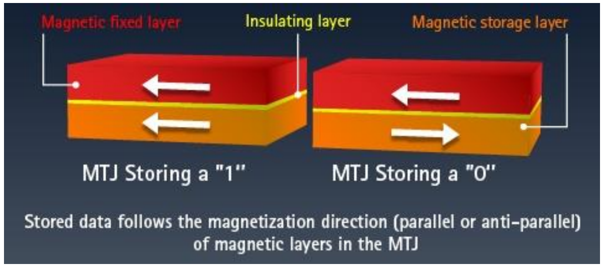
CoFeB → MgO → Co → Pd → Ru → PtMn → IrMn → Ta

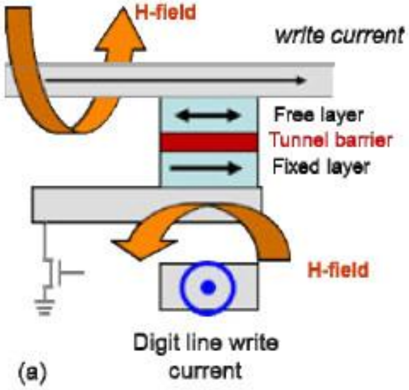
Magnetoresistive Radom Access Memory

MRAM vs. other memory devices

	SRAM	DRAM	FLASH	MRAM
Read	Fast	Moderate	Fast	Moderate-fast
Write	Fast	Moderate	Slow	Moderate-fast
Nonvolatile	No	No	Yes	Yes
Write Endurance	Unlimited	Unlimited	Limited	Unlimited
Cell size	Large	Small	Small	Small
Low voltage	Yes	Limited	No	Yes

🟧 Undesired attributes [1]



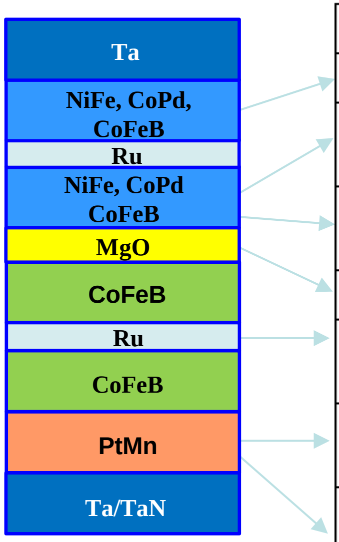


[2]

- MRAM provides nonvolatile storage, high read and write speeds, lower energy dissipation, and high write endurance
- The challenge in fabricating MRAM stack is hard to etch magnetic metal

[1] SMDL, Yonsei University Ceramic Engineering; [2] www.dailytech.com

Challenges in Patterning Magnetic Metal



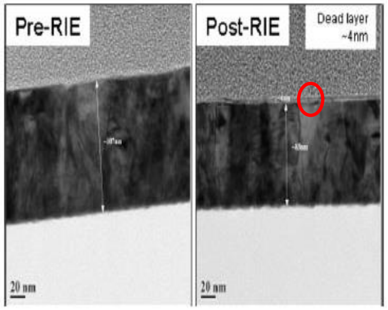
Potential chemistry for MRAM materials

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

Boiling point of metal halides [NIST,2013]

	Fluoride: T_B(°C)	Chloride:T_B(°C)
Ni	NiF_2 : 1750	$NiCl_{2(g)}$: unstable
Fe	$FeF_{2(g)}$: unstable $FeF_{3(g)}$: unstable	$FeCl_2$: 1023 $FeCl_3$: 316
Co	CoF_2 : 1400	$CoCl_2$: 1049
MgO	MgF_2 : 2260 OF_2 : -144	$MgCl_2$: 1412 OCl_2 : 11
Ru	RuF_5 : 227	$RuCl_3$: >500 (subl.)
Mn	MnF_2 : 1820	$MnCl_2$:1190
Pd	$PdF_{2(g)}$: unstable	$PdCl_{2(g)}$: unstable
Ta	TaF_5 : 229.5	$TaCl_5$: 242

Chemistry	Pros	Cons
Ion Milling (He, Ne, Ar)	Little or no chemical damage	Re-deposition → low density, electrical shorting; Low etch rate
C-O(X) based (CO/NH_3, CH_3OH**)**	Medium etch rate Better etch profile	Carbon layer deposition (2nm) after etch process
Halogen (Cl_2, BCl_3, SF_6)	Clean side walls High etch rate	Chemical corrosion → Magnetic degradation



Dead layer formation inducing magnetic property degradation after Cl_2 plasma [5]

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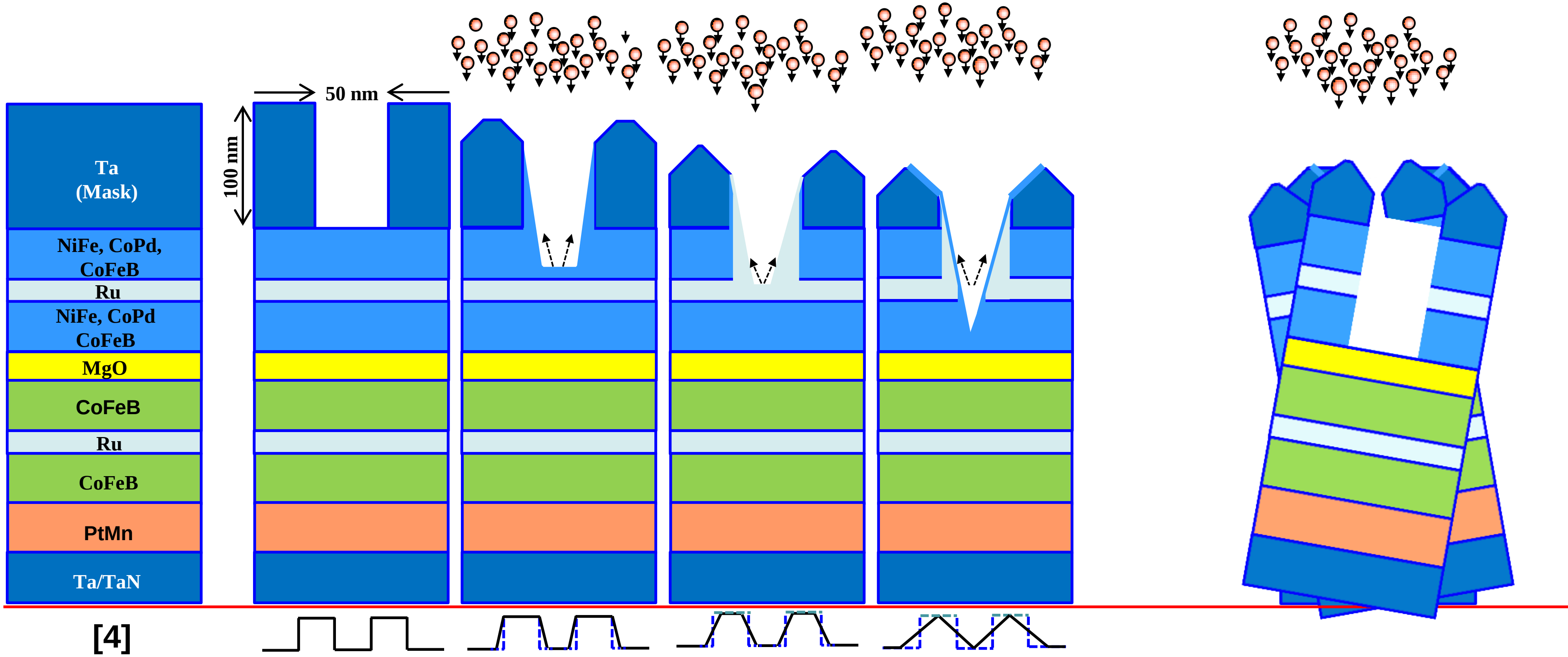
[3] K. Kinoshita et al. Jpn. J. Appl. Phys. 51 (2012) 08HA01, [4]] Kinoshita et al. JJAP 49 (2010) 08JB02-6, [5] J. Zhang, et al., JAP 107 (2010) 09A318

Sidewall Re-deposition



- **Physical sputtering results in sidewall re-deposition**
- **Ar ion in a tilt angle can remove the sidewall residue, but not for high- aspect ratio trench (6:1)**

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[6] J. M. Slaughter, Annu. Rev. Mater. Res., 39: 277-96, 2009

Method of Approach

Thermodynamic calculation to select viable etch chemistry

Co, Fe, and Ni film etch

- Volatility diagram
  - Single component plasma system (Cl_2, F_2, and Br_2)
  - Two components plasma system (Cl_2, F_2, Br_2, H_2 and O_2)
- Selecting optimized chemistry

Etch rate and XPS measurement

Application of selected chemistry to CoFe etch

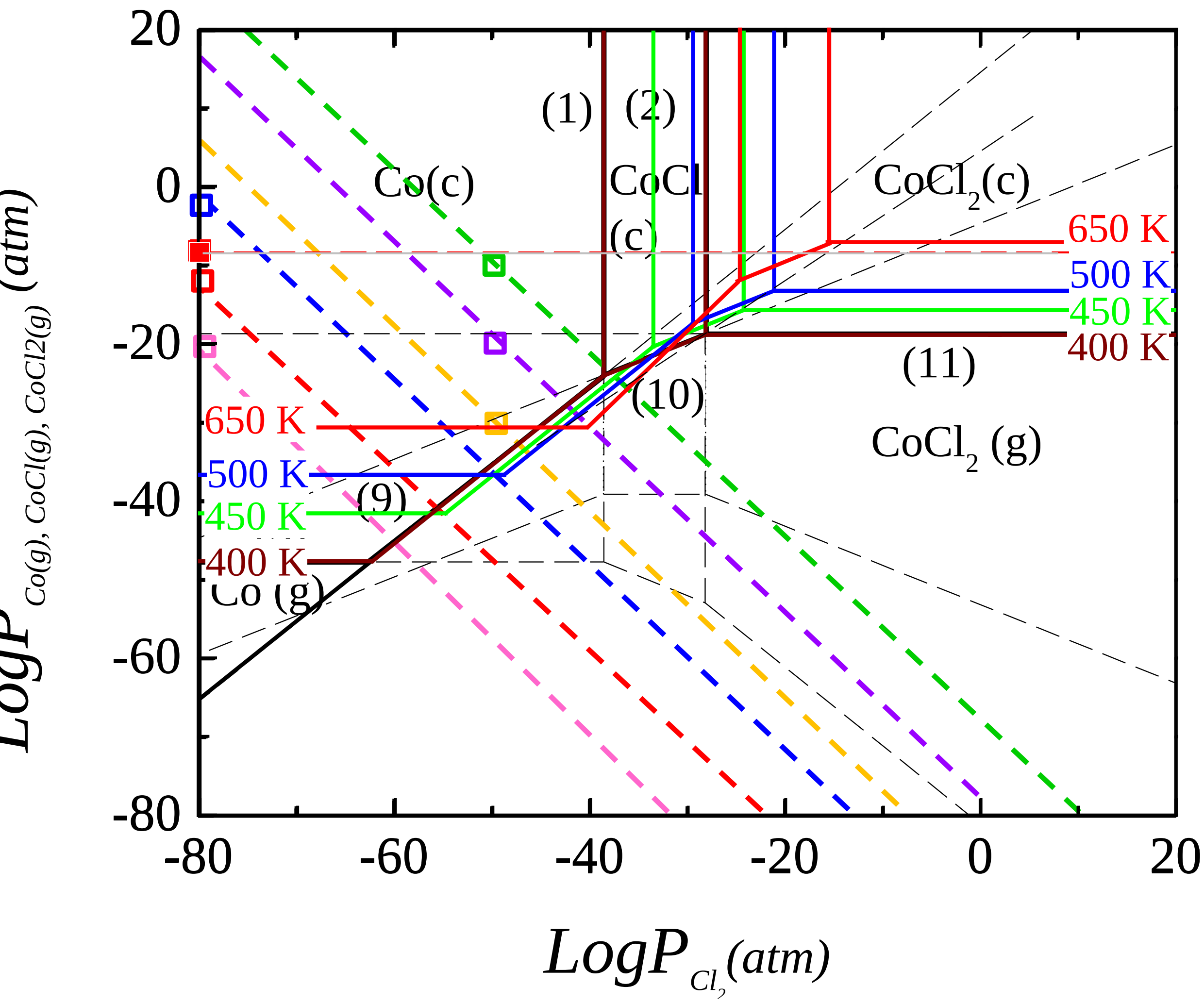
Surface analysis using XPS

- Metal chloride layer removal by hydrogen plasma.

Magnetic property (SQUID)

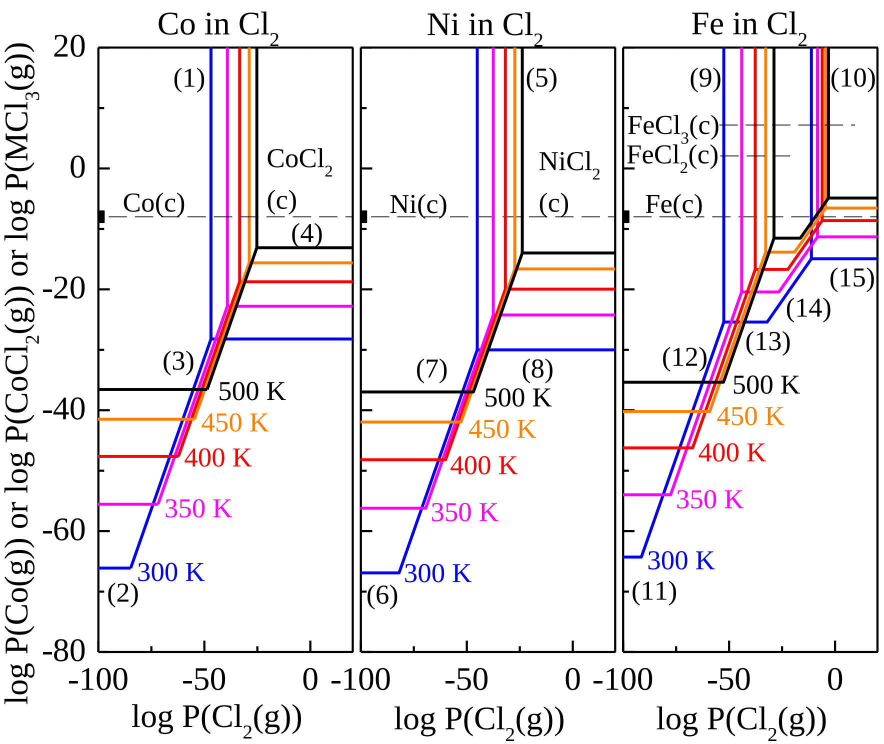
- Chemical degradation by Cl_2
- Recovery by H_2

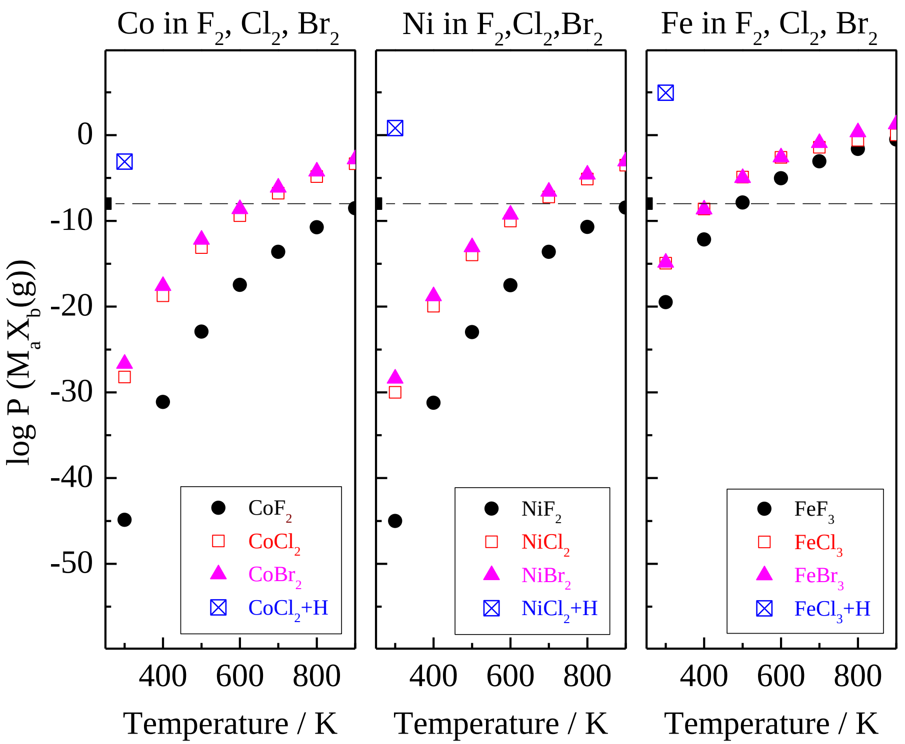
Volatility Diagram for Co-Cl_2 System



	Equilibrium between condensed phases
1	$Co(c) + 1/2Cl_2(g) \leftrightarrow CoCl(c)$
2	$CoCl(c) + 1/2Cl_2(g) \leftrightarrow CoCl_2(c)$
	Co(g) - condensed phases equilibrium
3	$Co(c) \leftrightarrow Co(g)$
4	$CoCl(c) \leftrightarrow Co(g) + 1/2Cl_2(g)$
5	$CoCl_2(c) \leftrightarrow Co(g) + Cl_2(g)$
	CoCl(g) - condensed phases equilibrium
6	$Co(c) + 1/2Cl_2(g) \leftrightarrow CoCl(g)$
7	$CoCl(c) \leftrightarrow CoCl(g)$
8	$CoCl_2(c) \leftrightarrow CoCl(g) + 1/2Cl_2(g)$
	$CoCl_2$(g) - condensed phases equilibrium
9	$Co(c) + Cl_2(g) \leftrightarrow CoCl_2(g)$
10	$CoCl(c) + 1/2Cl_2(g) \leftrightarrow CoCl_2(g)$
11	$CoCl_2(c) \leftrightarrow CoCl_2(g)$
	O(g) addition on $CoCl_2$(g)
12	$CoCl_2(c) + O(g) \rightarrow CoO(g) + Cl_2(g)$
13	$CoCl_2(c) + 3O(g) \rightarrow CoO(g) + 2OCl(g)$
	H(g) addition on $CoCl_2$(g)
14	$CoCl_2(c) + H(g) \rightarrow CoH(g) + Cl_2(g)$
15	$CoCl_2(c) + 3H(g) \rightarrow CoH(g) + 2HCl(g)$

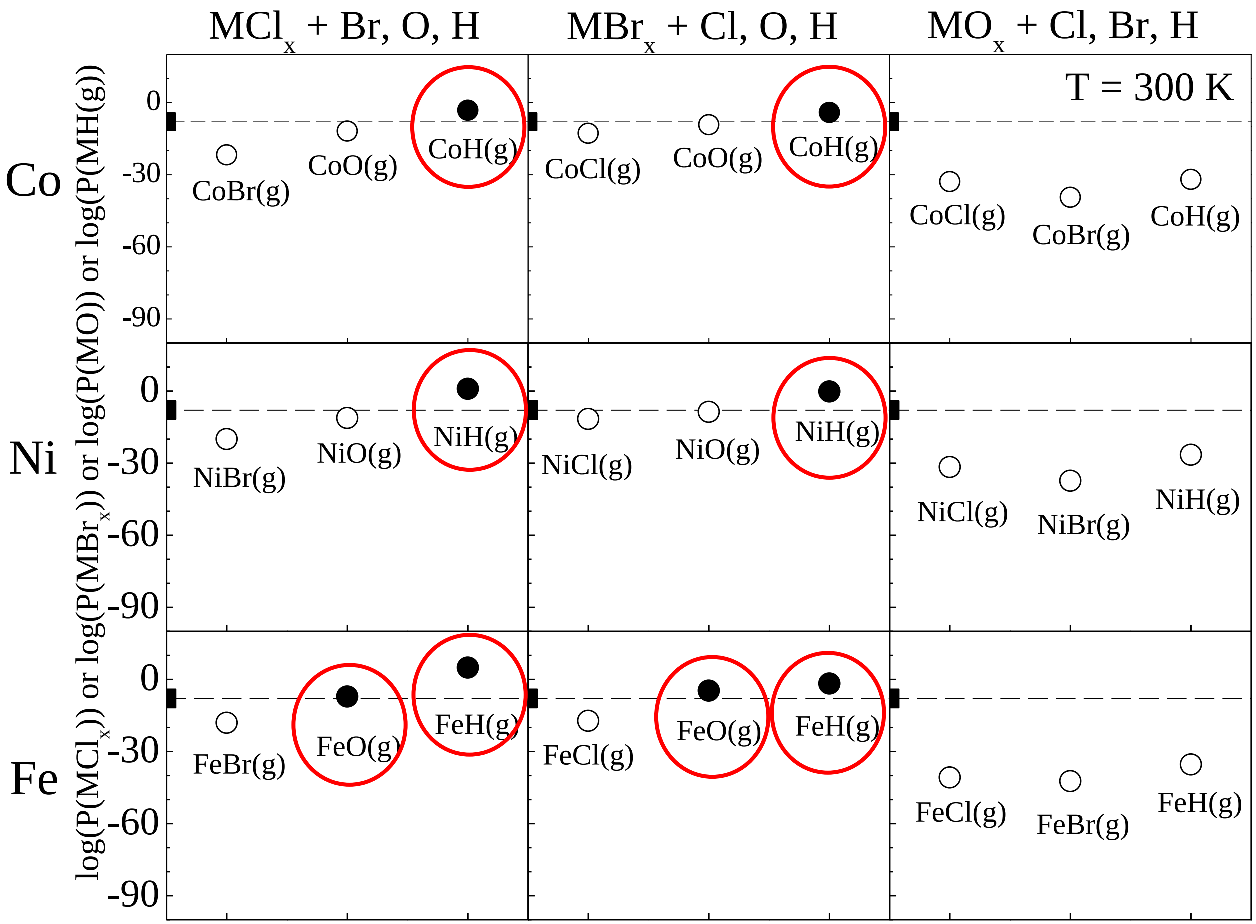
Volatility Diagram of Co/Ni/Fe-Cl_2





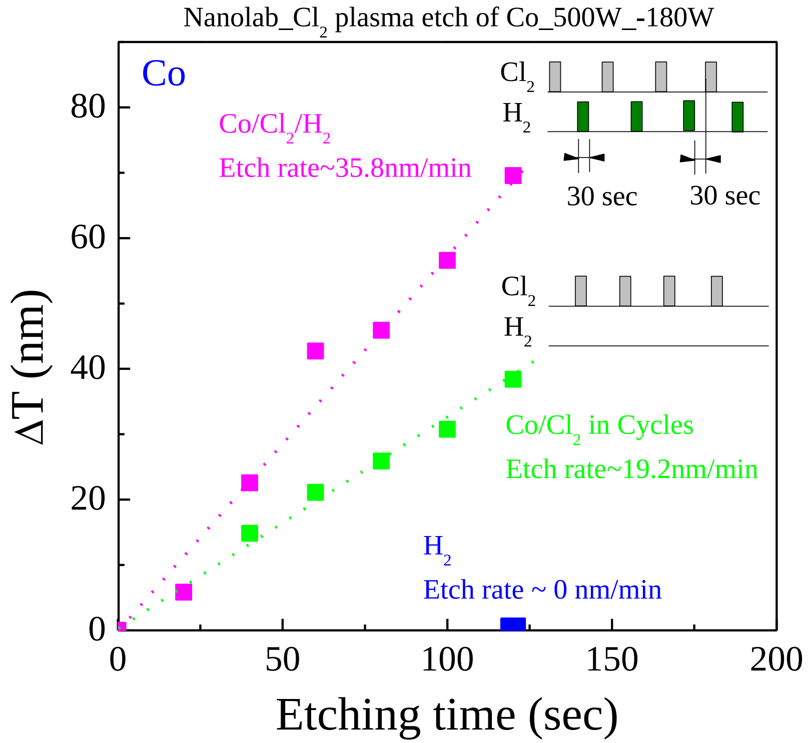
- **Based on volatility diagrams, the pressure of etch products, $CoCl_2$, $NiCl_2$ and $FeCl_3$, increases as increasing temperature**
- **The order of volatility: $FeCl_3 > CoCl_2 > NiCl_2$**

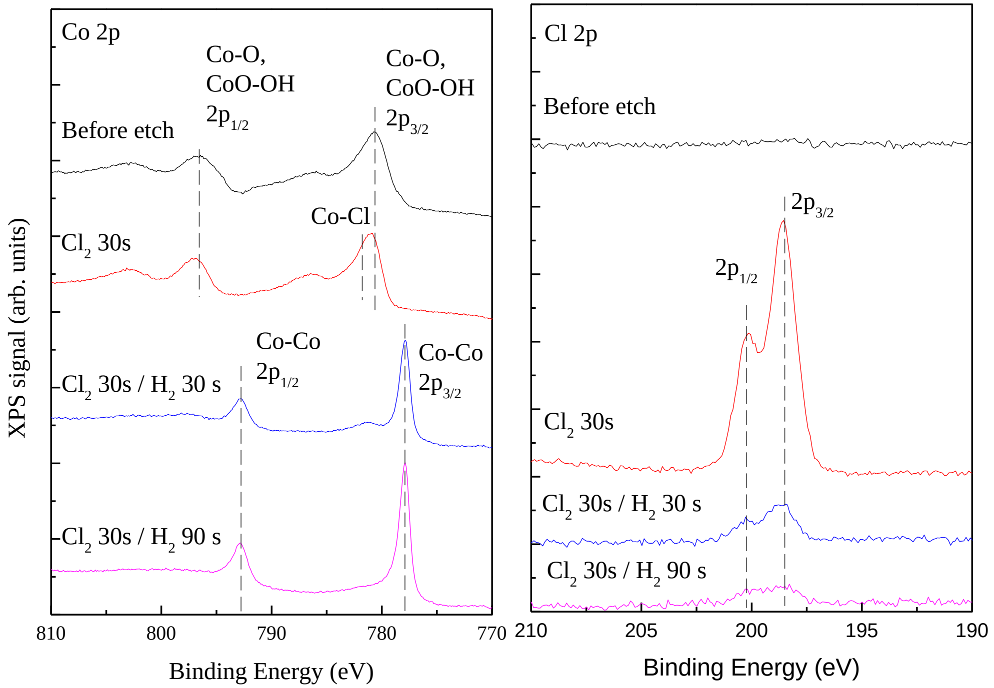
Evaluation of Sequential Chemistries



- **Cl/H and Br/H show pressure enhancement of etch products**

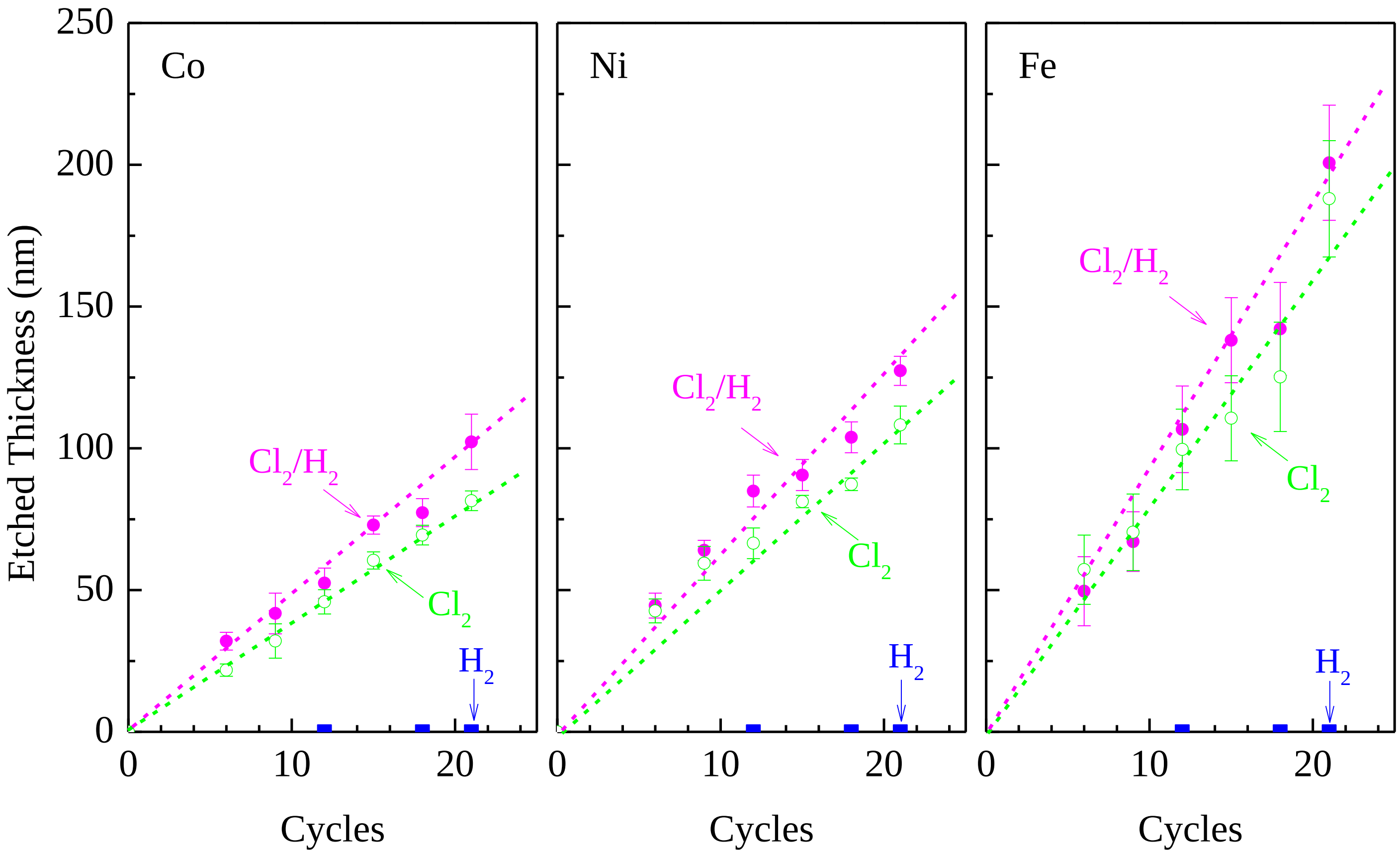
Co Etching by Cl_2/H_2





- **H_2 plasma addition enhances the etch rate of Co, which validates the thermodynamic calculation**
- **XPS results show metal chloride layer can be removed by H_2 plasma**

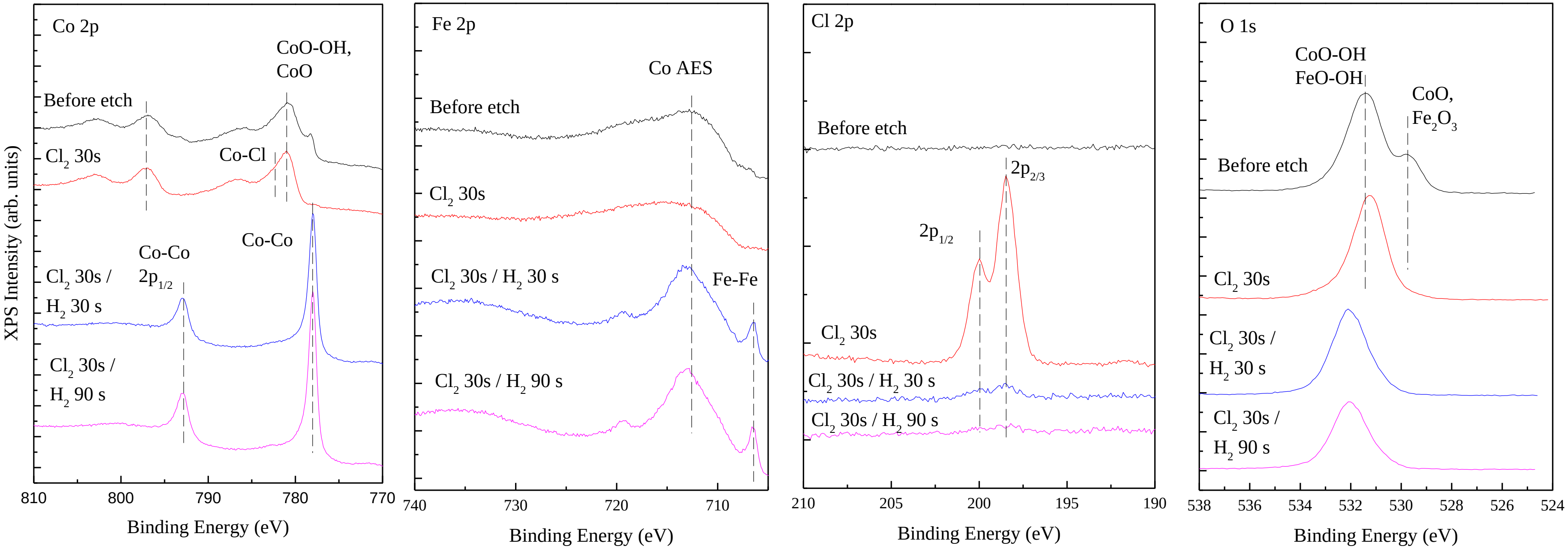
Co/Ni/Fe Etching by Cl_2/H_2



- **H_2 plasma addition enhances the etch rate of Co/Ni/Fe in Cl_2 plasma, which validates the thermodynamic calculation**

CoFe Alloy Etching by Cl_2/H_2

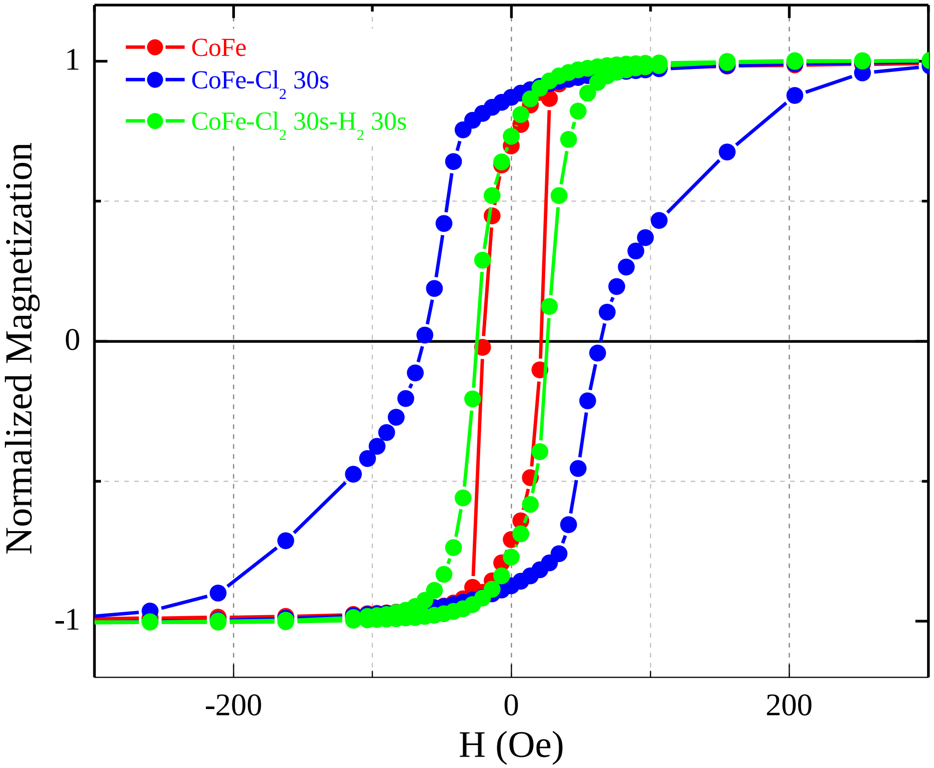
CoFe(1µm)



- **The Co-Cl and Fe-Cl peaks have been removed by H_2 plasma, resulting in metallic peak (Fe-Fe & Co-Co) in Co-2p and Fe-2p spectra**

Magnetic Properties of CoFe (Cl_2-H_2)

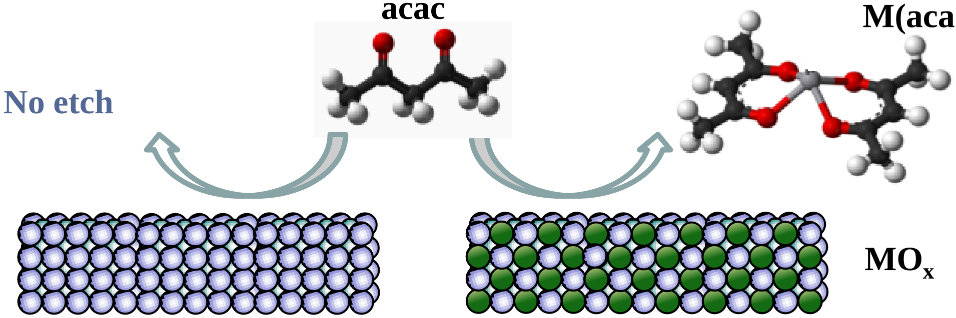
CoFe (45nm), M (H) (in-plane) at 300K



- **The degradation of magnetic property from Cl_2 plasma etch was restored by H_2 plasma treatment**

Effect of Surface States

$M(acac)_n$ vaporization induced by acac exposure on metal oxide surfaces



acac

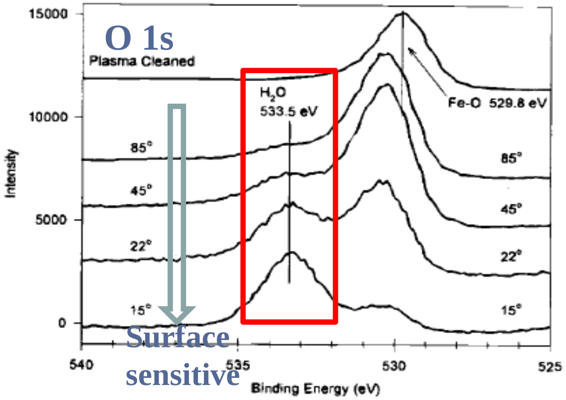
No etch

$M(acac)_2$

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

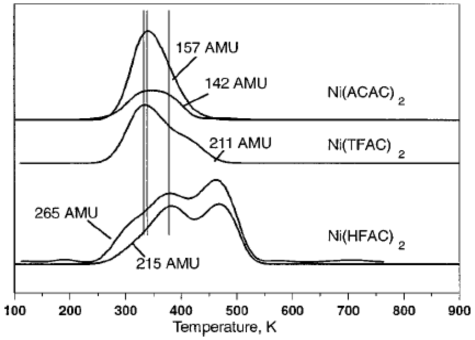
MO_x

[7] Fe_2O_3 + 6Hhfac → 2Fe $(hfac)_3$ + $6H_2O$

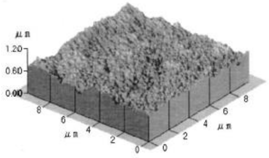


[8] $Ni(acac)_2$, $Ni(tfac)_2$, and $Ni(hfac)_2$

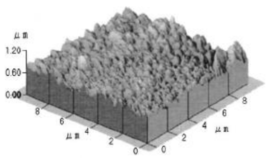
Acac / Ni , TPD, Ts = 100 K



[9] Roughness change of CuO_x film



Before Hfac
RMS roughness :
50 nm

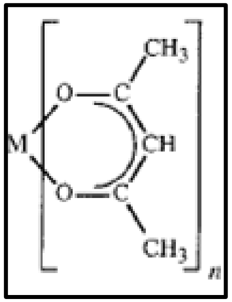


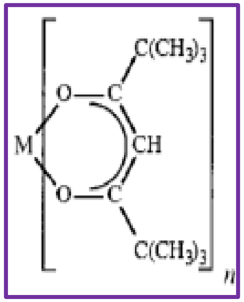
After Hfac
RMS roughness :
90 nm

[7] D. W. Hess et al ECS 142 (1995) 961 ; [8] R. I. Masel et al. JVST A. 16 (1998) 3259; [9] S.W. Kang et al. JVST B. 17 (1999) 154

Other Potential Chemistries

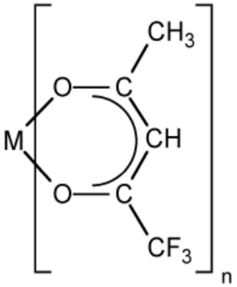
Acetylacetonate (ACAC)

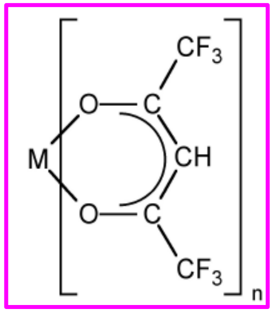




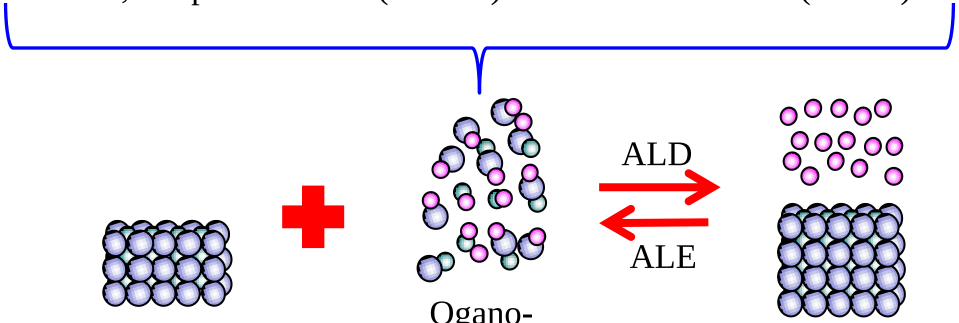
2,2,6,6-tetra-methyl-3,5-heptanedionate (TMHD)

Triuoroacetylacetonate (TFAC)





hexauoroacetylacetonate (HFAC)



Metal film

Ogano-metallic chemistry

Metal film

- **“Reverse engineering” of ALD points to organo-metallic chemistry as a viable alternative to halogens**

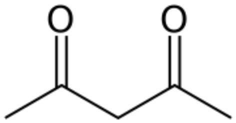
Product	**MP (°C)**	**BP/T$_{sub}$(°C)**	**Vapor pressure @ 150°C (Torr)**
$CoCl_2$	737	1049	-
$CoCO_3$	**280***		-
$Co_2(CO)_8$	**51***		-
$Co_4(CO)_{12}$	**60***		-
$Co(acac)_2$	170	181 (exp~200)	-
$Co(acac)_3$	211	170 (exp~190)	1.059
$Co(tmhd)_2$	254	171 (exp~192)	-
$Co(tmhd)_3$	143	161 (exp~179)	-
$Co(tfac)_3$	-	131	3.319
$Co(hfac)_3$	-	90	9.132
$FeCl_3$	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)	2.781
$Fe(tmhd)_3$	164	150 (exp~177)	-
$Fe(tfac)_3$	-	121	8.34
$Fe(hfac)_3$	-	81	25.021
$NiCl_2$	1031	985 (subl)	-
$Ni(CO)_4$	**-19**	**42 (exp~60)**	

[5] NIST, 2012

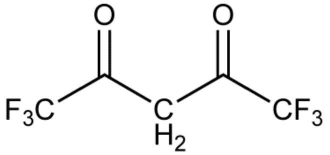
[10] A. R. Barron, Creative Commons Attribution License, Connexions module: m33649

Reverse Engineering

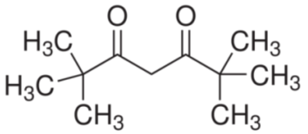
acac (Acetylacetone)

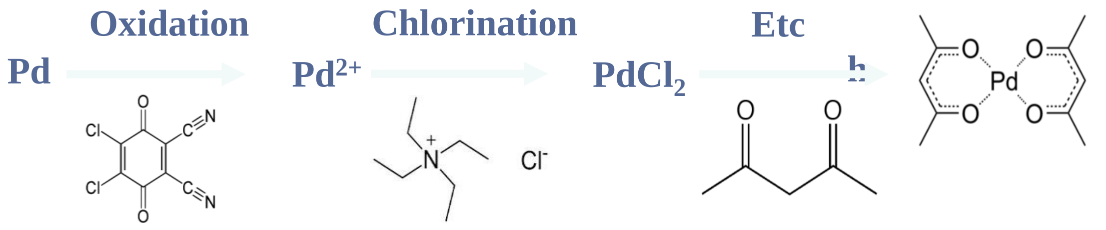


hfac (Hexafluoroacetylacetone)



tmhd (Tetramethyl heptanedione)





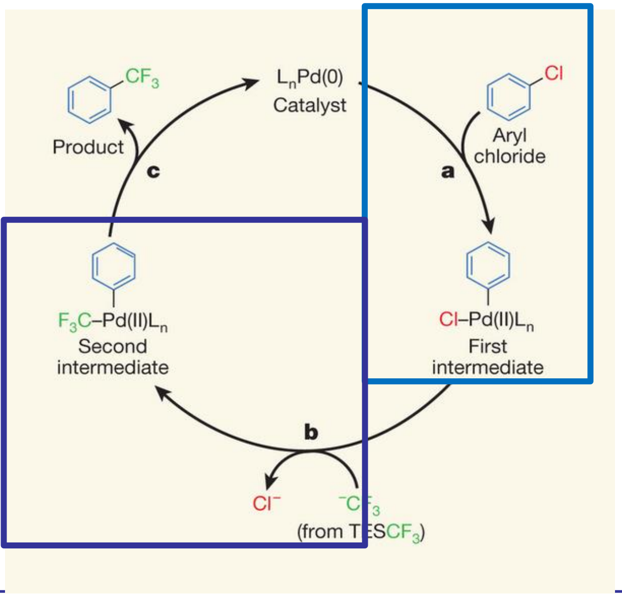
Pd —Oxidation→ **Pd^{2+}** —Chlorination→ **$PdCl_2$** —Etc→

2,3-dichloro-5,6-dicyano-p-benzoquinone (ddq)

tetraethyl ammonium chloride

Acetyl acetonate

Pd - organometallic compounds



Catalytic cycle to demonstrate chemistry

Pd breaks Cl-organic bond

Pd-Cl bond replaced with Pd-organic bond

Plan to keep acac/hfac as organics or borrow from Cl source

- Cl is a good leaving group and can be replaced with organics for volatility

Reference

[1] SMDL, Yonsei University Ceramic Engineering
[2] www.dailytech.com
[3] K. Kinoshita et al. Jpn. J. Appl. Phys. 51 (2012) 08HA01
[4] Kinoshita et al. JJAP 49 (2010) 08JB02-6
[5] J. Zhang, et al., JAP 107 (2010) 09A318
[6] J. M. Slaughter, Annu. Rev. Mater. Res., 39: 277-96, 2009
[7] D. W. Hess et al ECS 142 (1995) 961
[8] R. I. Masel et al. JVST A. 16 (1998) 3259
[9] S.W. Kang et al. JVST B. 17 (1999) 154
[10] A. R. Barron, Creative Commons Attribution License, Connexions module: m33649

Industrial Interactions and Technology Transfer

- Conference call with Intel, January 10, 2013, (Satyarth Suri)
- Conference call with Intel, February 21, 2013, (Satyarth Suri)
- Visit Intel, Portland, OR, April, 3, 2013, (Bob Turkot, Satyarth Suri)
- Conference call with SRC, April 24, 2013 (Bob Haveman)
- Conference call with Intel, May 16, 2013, (Satyarth Suri)
- Conference call with Intel, June 13, 2013, (Satyarth Suri)
- Conference call with Intel, July 18, 2013, (Satyarth Suri)
- Conference call with Intel, August 29, 2013, (Satyarth Suri)
- Conference call with Intel, October 10, 2013, (Satyarth Suri)
- Conference call with Intel, November 14, 2013, (Satyarth Suri)
- Conference call with Intel, February 13, 2014, (Satyarth Suri)
- Conference call with Intel, March 20, 2014, (Satyarth Suri)

Future Plans

Next Year Plans

- Perform thermodynamic calculations to assess potential impact and projected effectiveness
- Improve MTJ etch by investigating bulky organic ligands which generate high volatile etch products

Long-Term Plans

- Formulate the models to predict etch product from plasma processes
- Propose plasma chemistries via thermodynamic calculation

Publications, Presentations, and Recognitions/Awards

Presentation:

- **Contributed talk at AVS International Symposium, October 2013**
  (T. Kim, J. K. Chen and J. P. Chang, “Thermodynamic Approach to Select Viable Etch Chemistry for Magnetic Metals”)

- **Contributed talk at AIChE Annual Meeting, October 2013**
  (J. K. Chen and J. P. Chang, “Selection of non-PFC Chemistries for Through-Silicon via Etch”)
  (T. Kim, J. K. Chen and J. P. Chang, “Thermodynamic Approach to Select Viable Etch Chemistry for Magnetic Metals”)

Publication:

- **Deliverable Report, P065582, “Non-PFC Plasma Chemistries for Patterning Complex Materials/Structures”, January 2014**
- **Pre-print, “Thermodynamic Assessment and Experimental Verification of Reactive Ion Etching of Magnetic Metal Elements,” submitted to SRC for review**