Alternative Etchants for Magnetic Materials

(*Task Number: 425.046*)

PIs:

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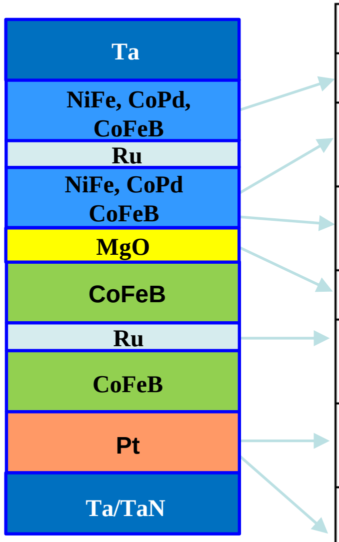
Challenges in Patterning Magnetic Metal


Ta
NiFe, CoPd, CoFeB
Ru
NiFe, CoPd CoFeB
MgO
CoFeB
Ru
CoFeB
Pt
Ta/TaN

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

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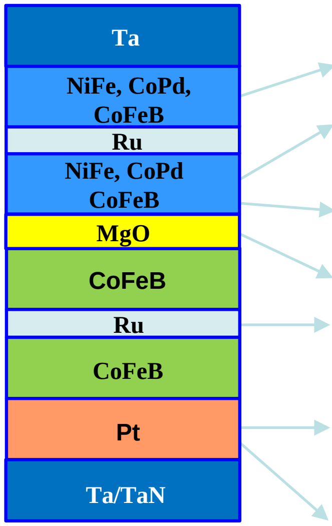
[1] K. Kinoshita et al. Jpn. J. Appl. Phys. 51 (2012) 08HA01, [2] Kinoshita et al. JJAP 49 (2010) 08JB02-6, [3] J. Zhang, et al., JAP 107 (2010) 09A318

Challenges in Patterning Magnetic Metal



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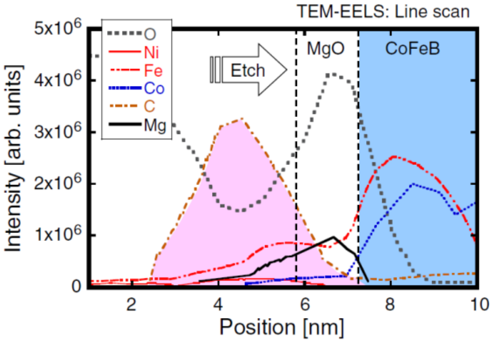

C-layer formation after CH_3OH/Ar plasma [4]

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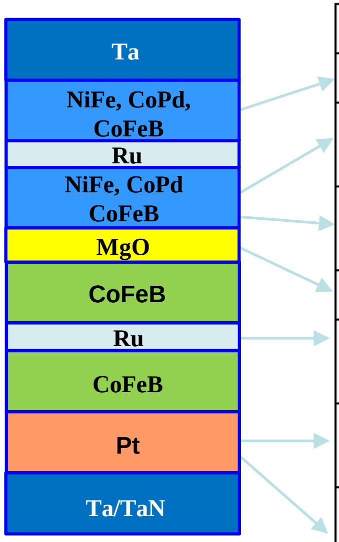

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NiFe, CoPd, CoFeB

Ru

NiFe, CoPd CoFeB

MgO

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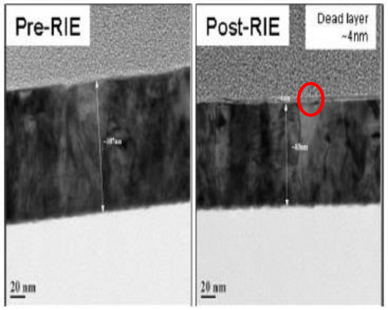

Dead layer formation inducing magnetic property degradation after Cl_2 plasma [5]

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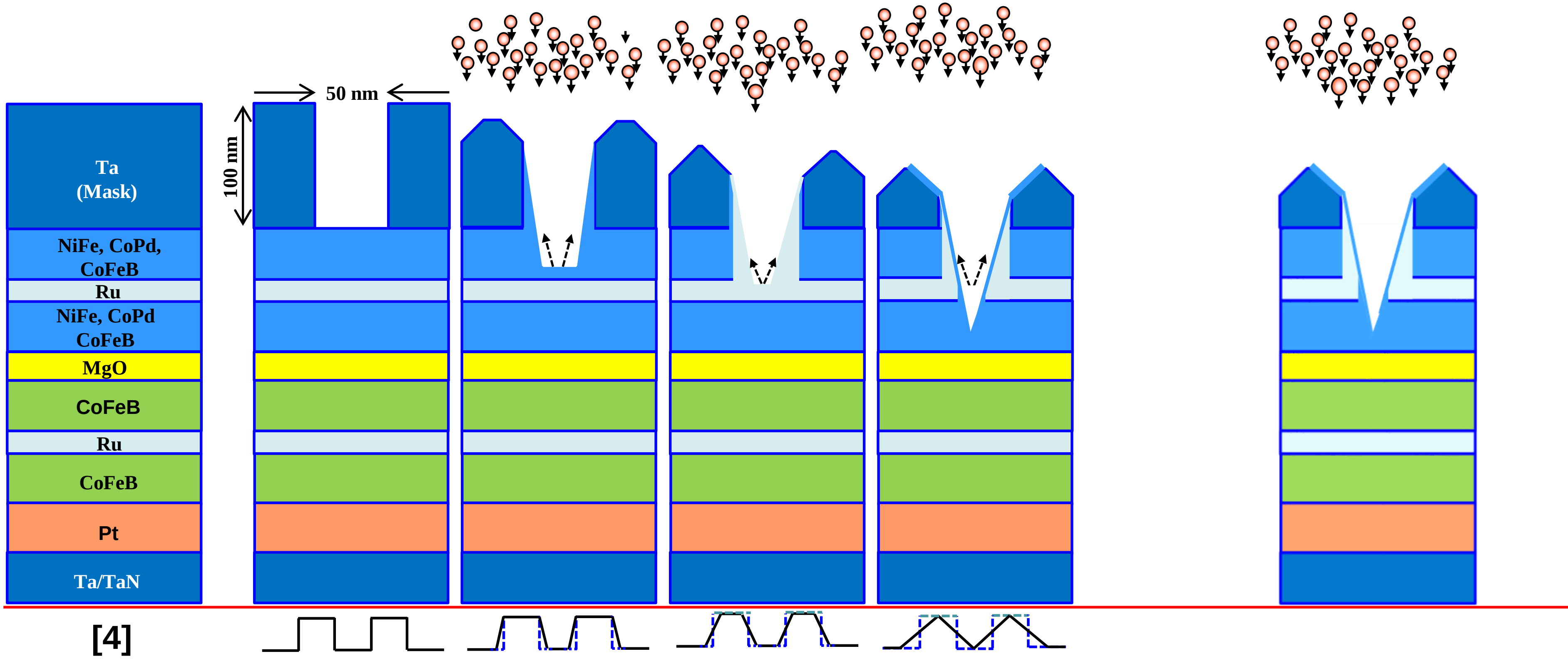
Sidewall Re-deposition



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

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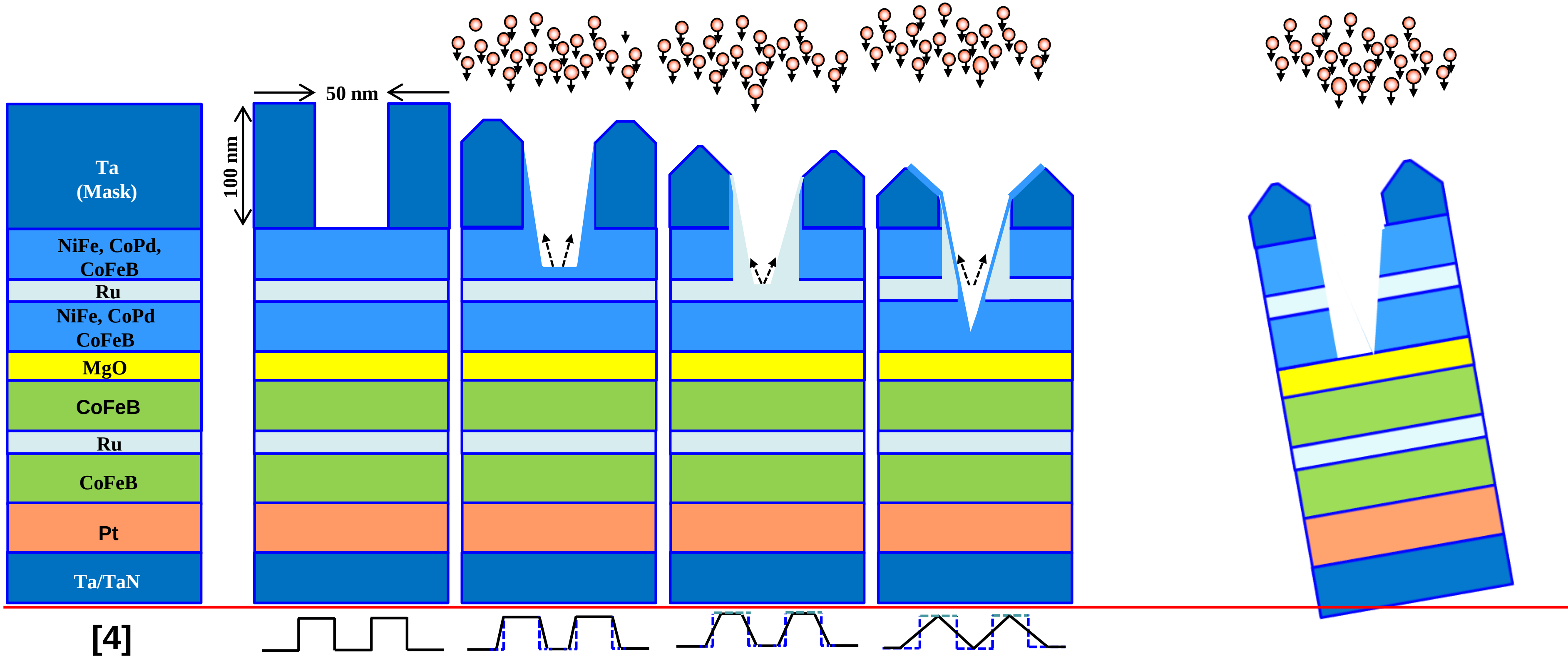

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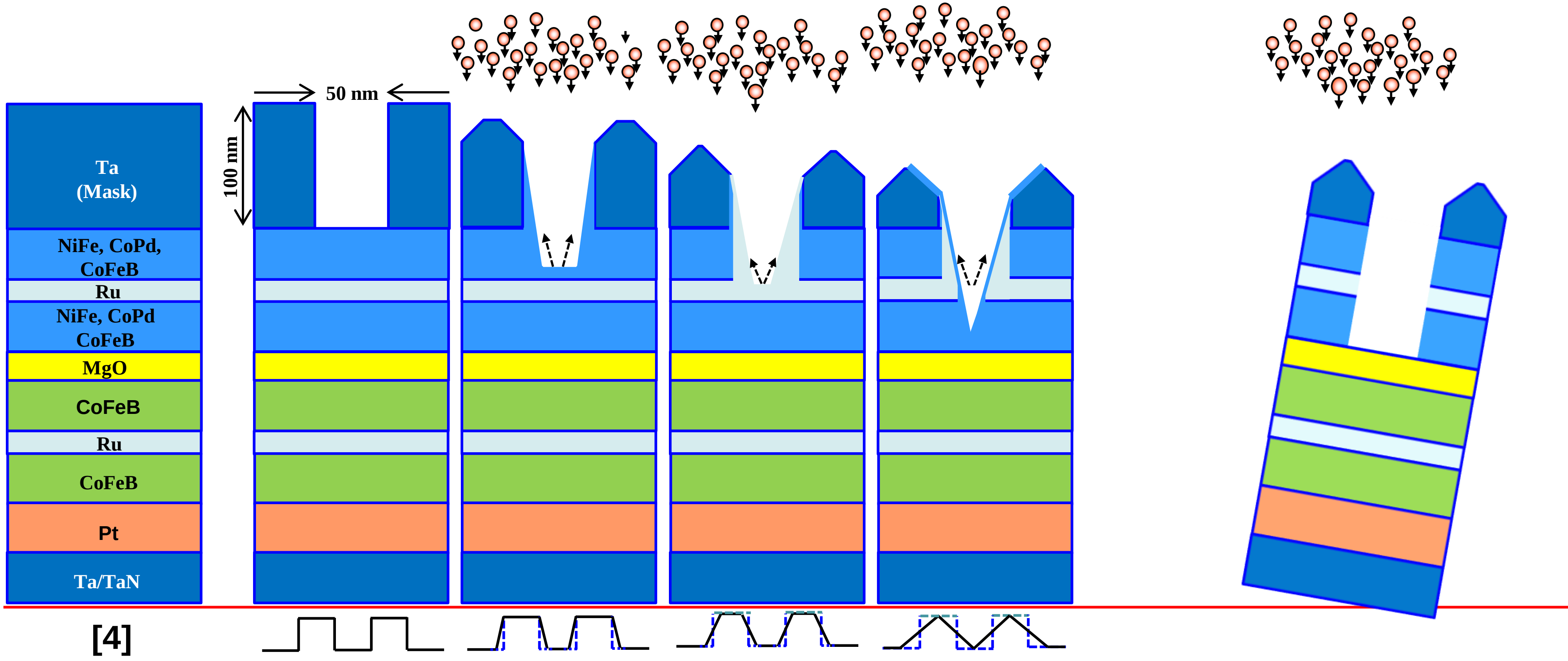

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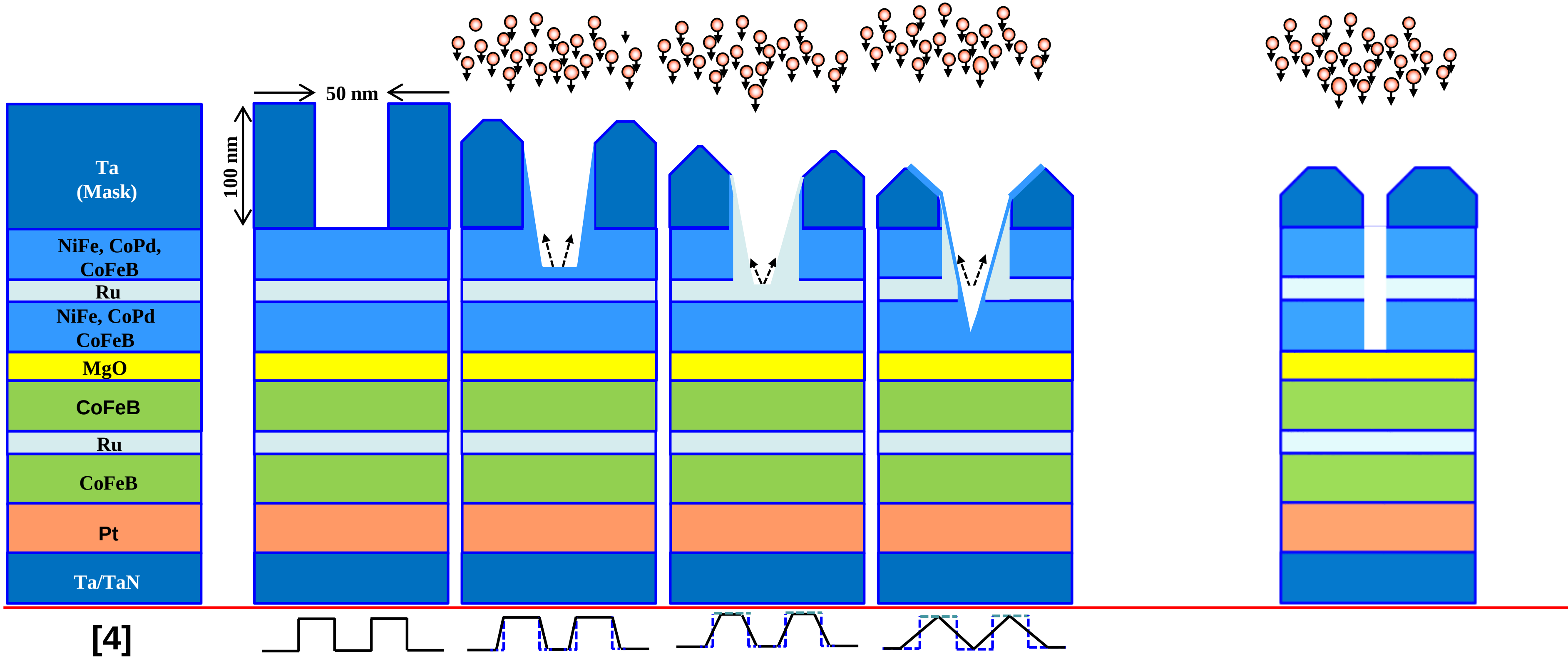

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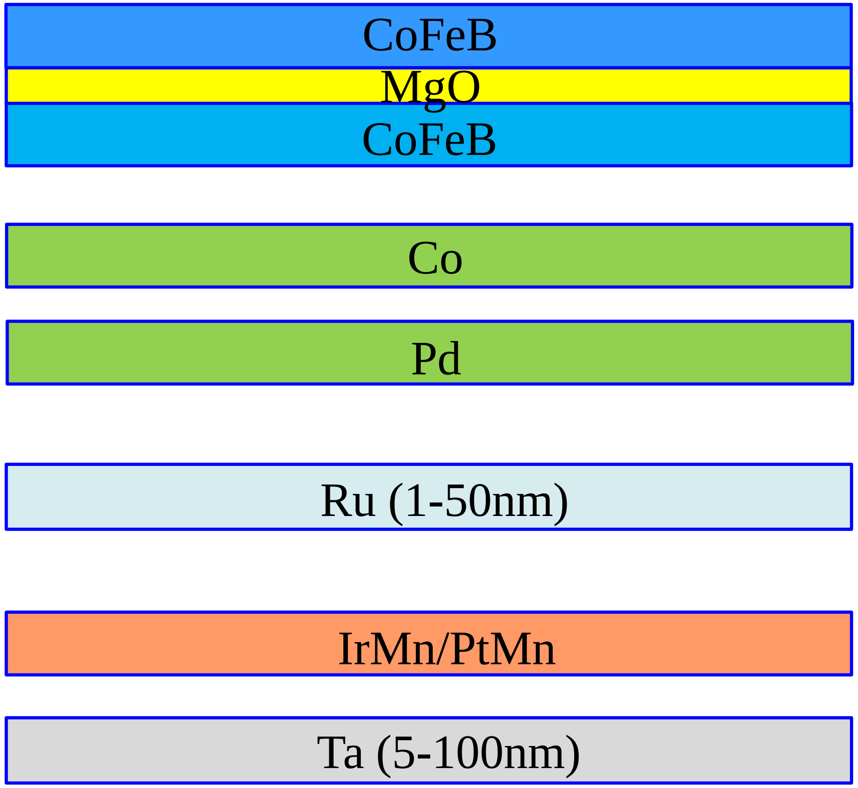
Target of MRAM Metal Etch

2014 Specified Metrics

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

Target of MRAM Metal Etch

2015 Specified Metrics

Intel specified metrics:

CoFeB

- Conservation of magnetic properties

Pt

- Identification of effective etching chemistry

Cu

- Transition from CMP to plasma processing

Re-alignment to focus on:

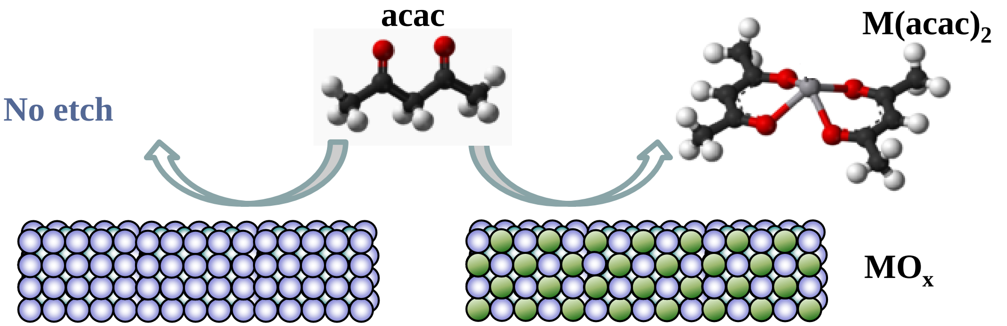
1	Co-based, Pt, and Cu metallic films
2	Advancement towards atomic layer etch of hard-to-pattern materials
3	Easily etched via halide chemistry? →Volatility analysis

Priority of research:

CoFeB → Pt → Cu

Effect of Surface States

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



acac

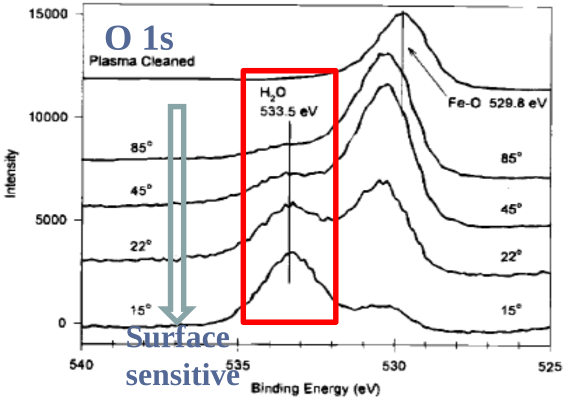
No etch

$M(acac)_2$

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

MO_x

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

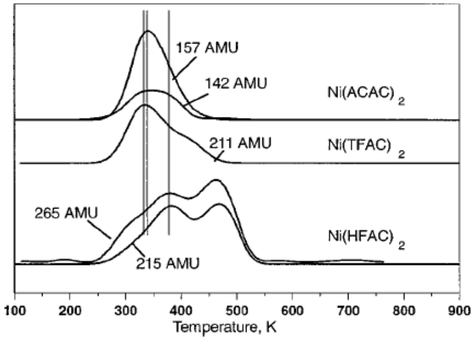


O 1s

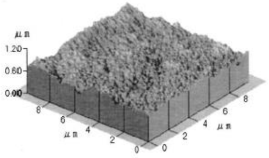
Surface sensitive

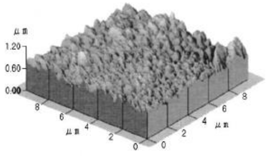
[8] $Ni(acac)_2$, $Ni(tfac)_2$, and $Ni(hfac)_2$

Acac / Ni , TPD, Ts = 100 K



[9] Roughness change of CuO_x film





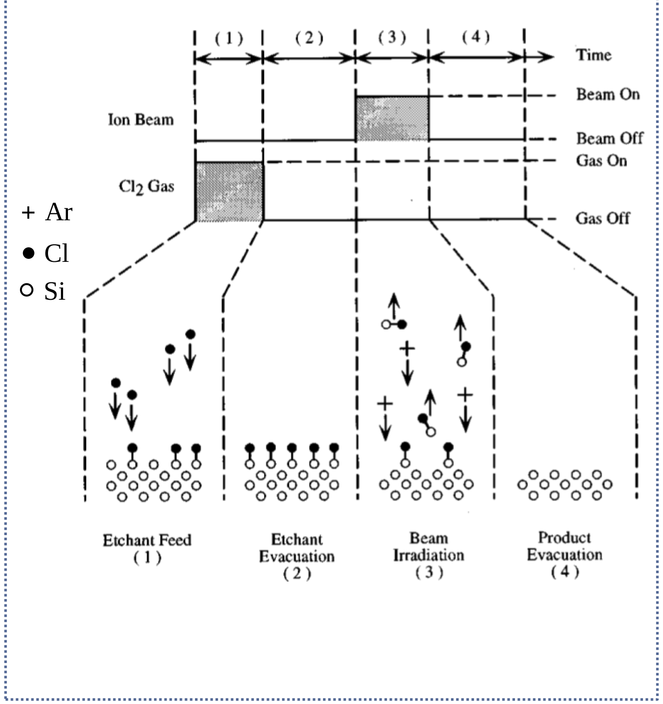
Before Hfac
RMS roughness :
50 nm

After Hfac
RMS roughness :
90 nm

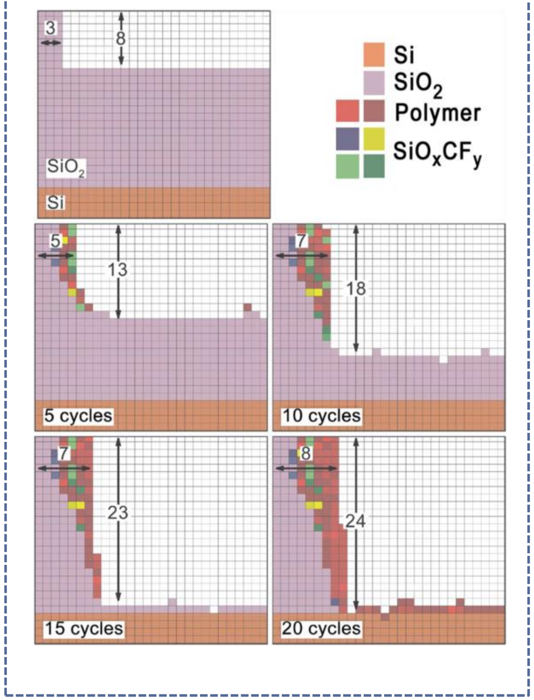
[7] D. W. Hess et al ECS 142 (1995) 961 ; [8] R. I. Masel et al. JVST A. 16 (1998) 3259; [9] S.W. Kang et al. JVST B. 17 (1999) 154

Atomic Layer Etch (ALE)

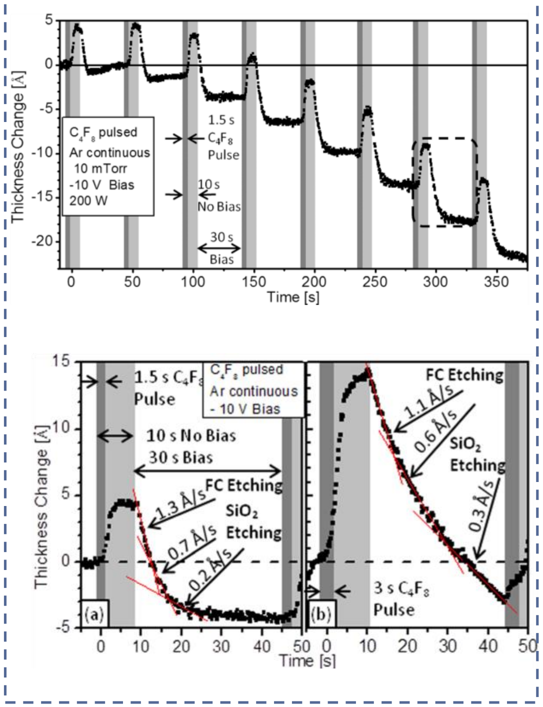
Si (Economou 1995)



SiO_2 (Kushner 2004)



SiO_2 (Oehrlein 2014)



- **Atomic layer etch of Si (1995) achieved through sequence of monolayer chlorination and Ar^+ bombardment**
- **ALE of SiO_2 simulated (2004) and confirmed experimentally by pulsed C_4F_8 with continuous Ar irradiation (2014)**

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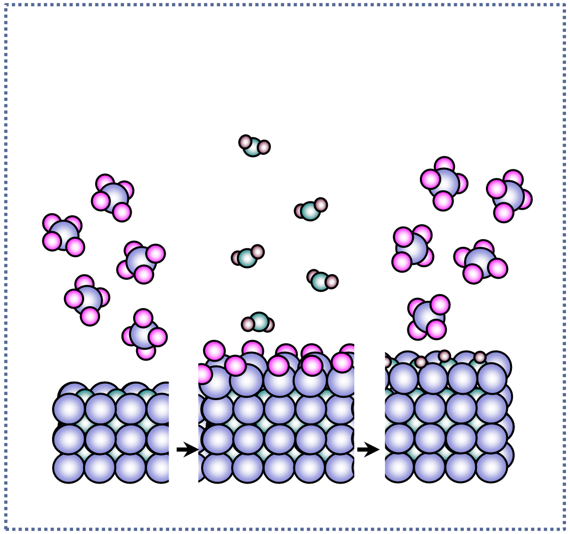
[5] S.D. Athavale, D.J. Economou, JVST A, 13, 966-971 (1995), [6] A. Agarwal, M.J. Kushner, JVST A, 27, 37 (2009), [7] D. Metzler, *et al.*, JVST A, 32, 020603 (2014).

Strategy for ALE

ALD

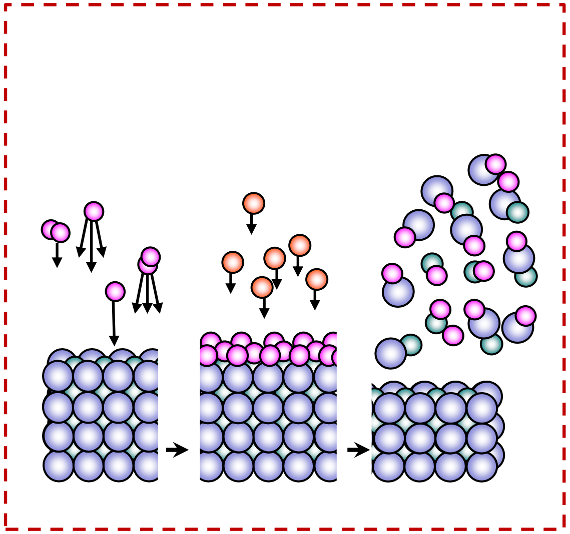


Half Reactions for ALD of MO_2:

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

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

ALE



Half Reactions for ALE of M_xO_y:

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

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

- **Self limiting nature of ALD process comes from transformation and subsequent regeneration of surface species**
- **Current strategy to reverse ALD, requiring only single self-limiting surface functionalization step**

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

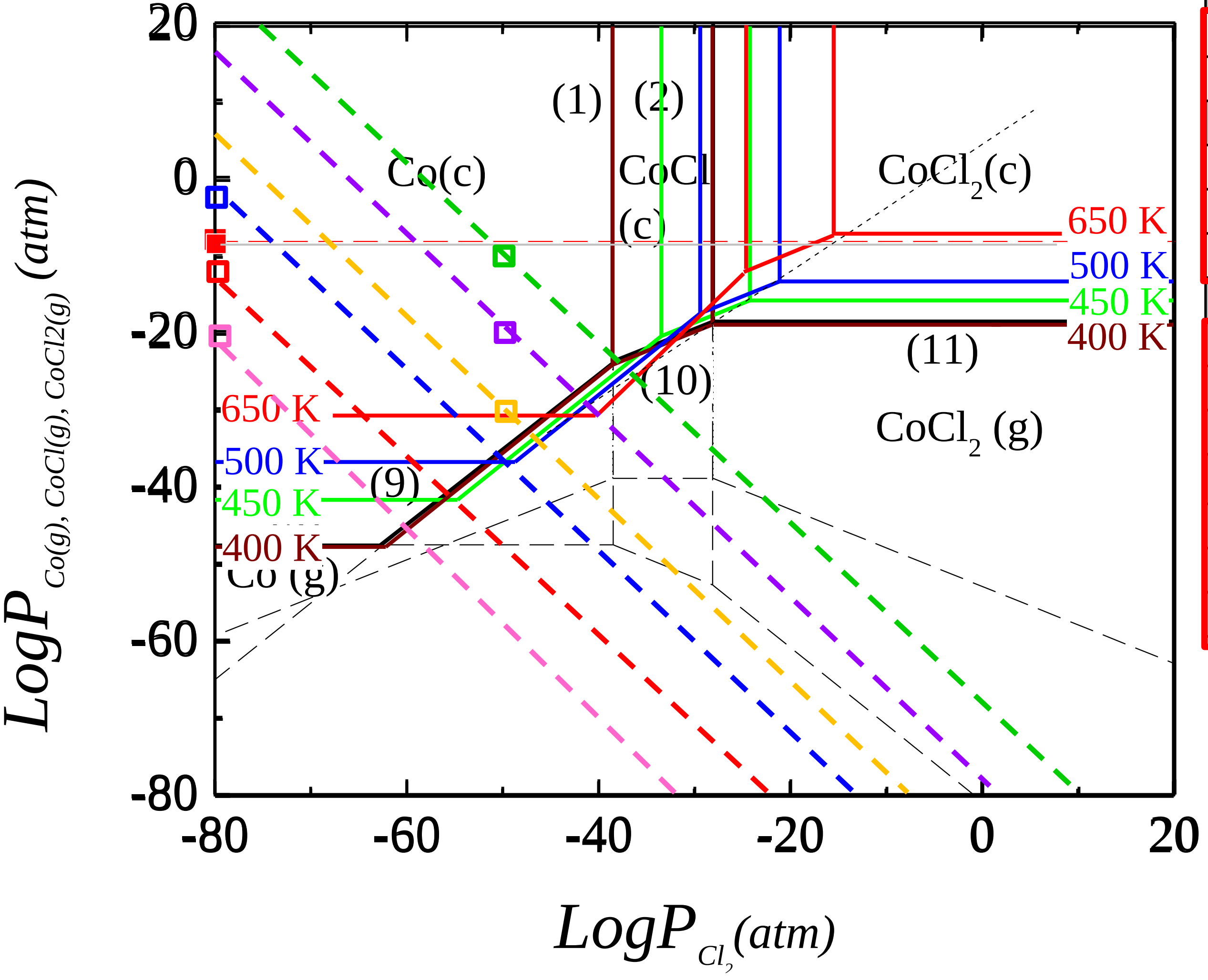
Surface analysis using XPS

- 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) ↔ CoCl(c)
2	CoCl(c) + 1/2Cl_2(g) ↔ $CoCl_2$(c)
	Co(g) - condensed phases equilibrium
3	Co(c) ↔ Co(g)
4	CoCl(c) ↔ Co(g) + 1/2Cl_2(g)
5	$CoCl_2$(c) ↔ Co(g) + Cl_2(g)
	CoCl(g) - condensed phases equilibrium
6	Co(c) +1/2Cl_2(g) ↔ CoCl(g)
7	CoCl(c) ↔ CoCl(g)
8	$CoCl_2$(c) ↔ CoCl(g) +1/2Cl_2(g)
	$CoCl_2$(g) - condensed phases equilibrium
9	Co(c)+ Cl_2(g) ↔$CoCl_2$(g)
10	CoCl(c)+ 1/2Cl_2(g) ↔ $CoCl_2$ (g)
11	$CoCl_2$(c) ↔ $CoCl_2$(g)

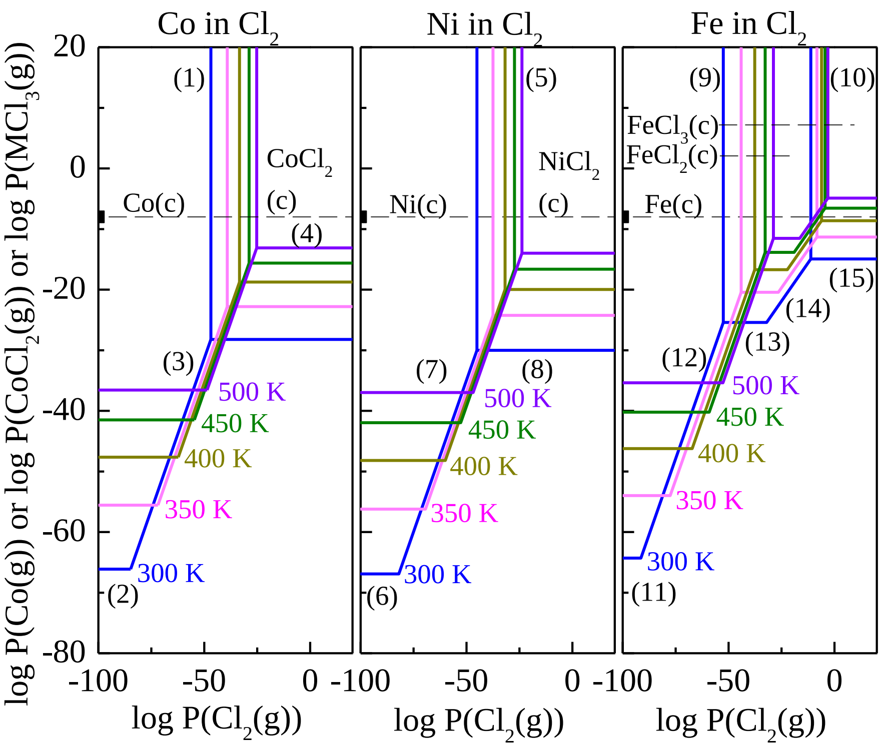
$CoCl_2$(c) + O(g) → CoO(g) + Cl_2(g)

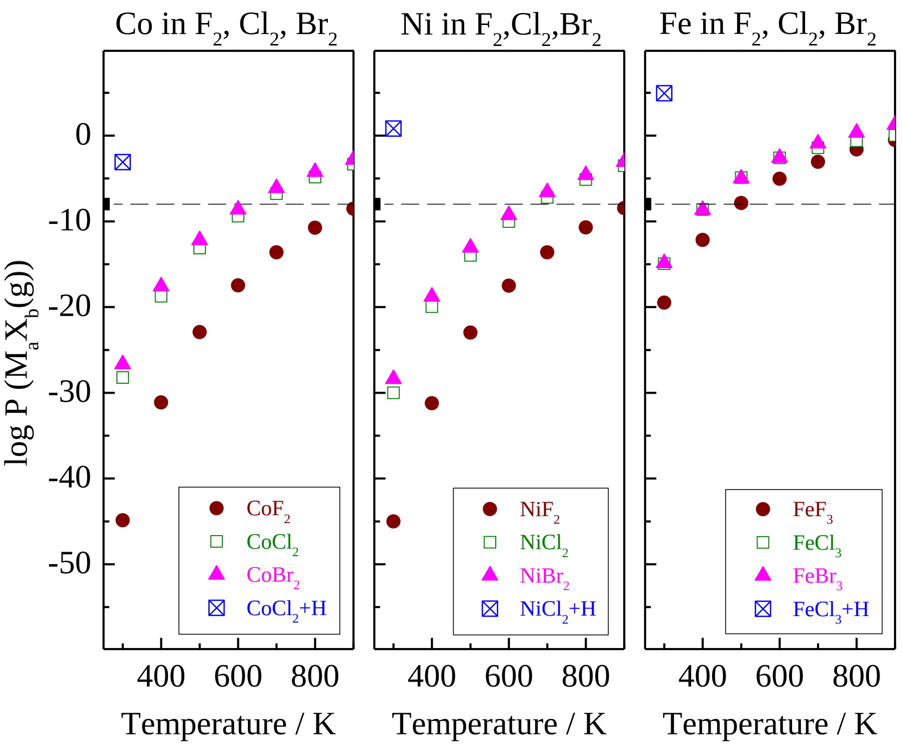
$CoCl_2$(c) + 3O(g) → CoO(g) + 2OCl(g)

$CoCl_2$(c) + H(g) → CoH(g) + Cl_2(g)

$CoCl_2$(c) + 3H(g) → CoH(g) + 2HCl(g)

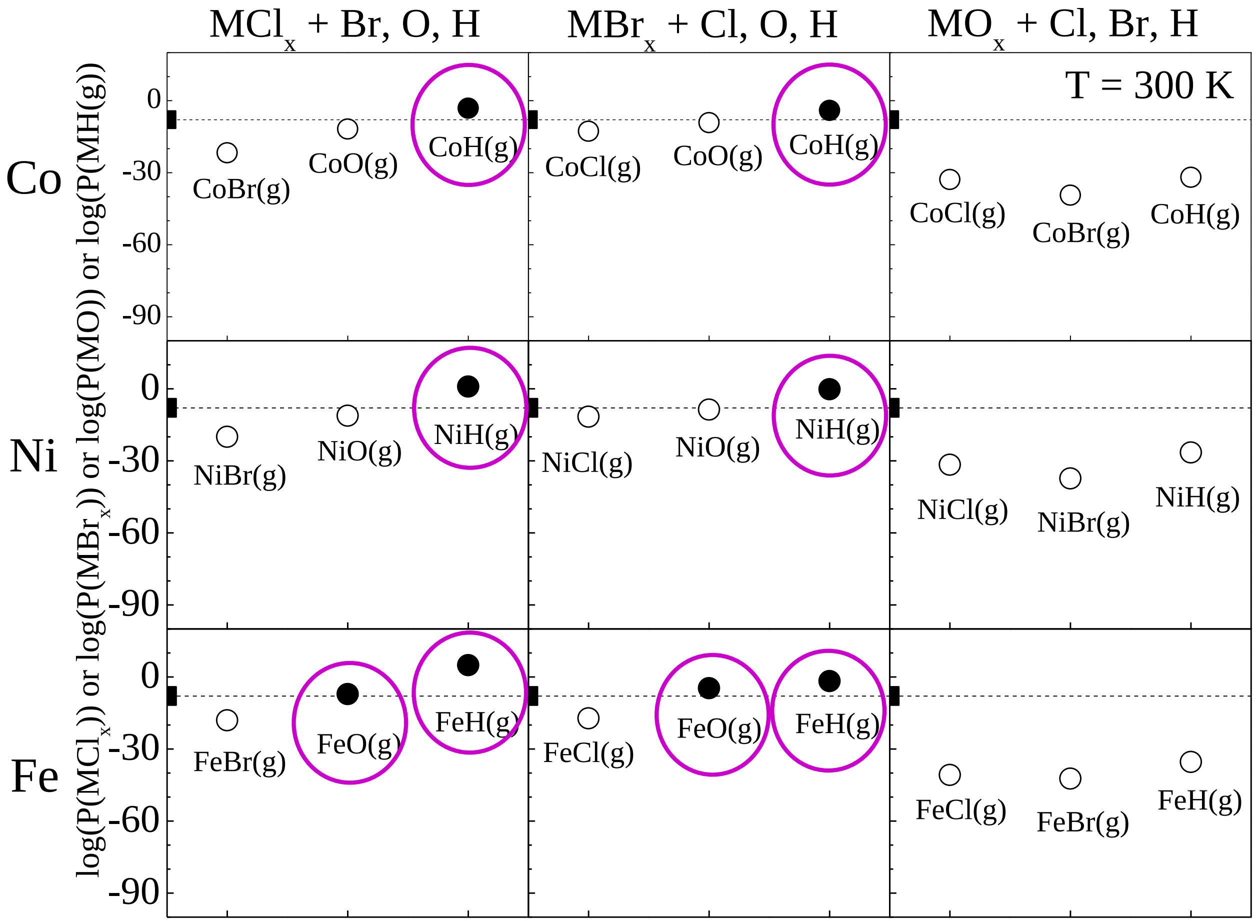
Volatility Diagram of Co/Ni/Fe-Cl_2





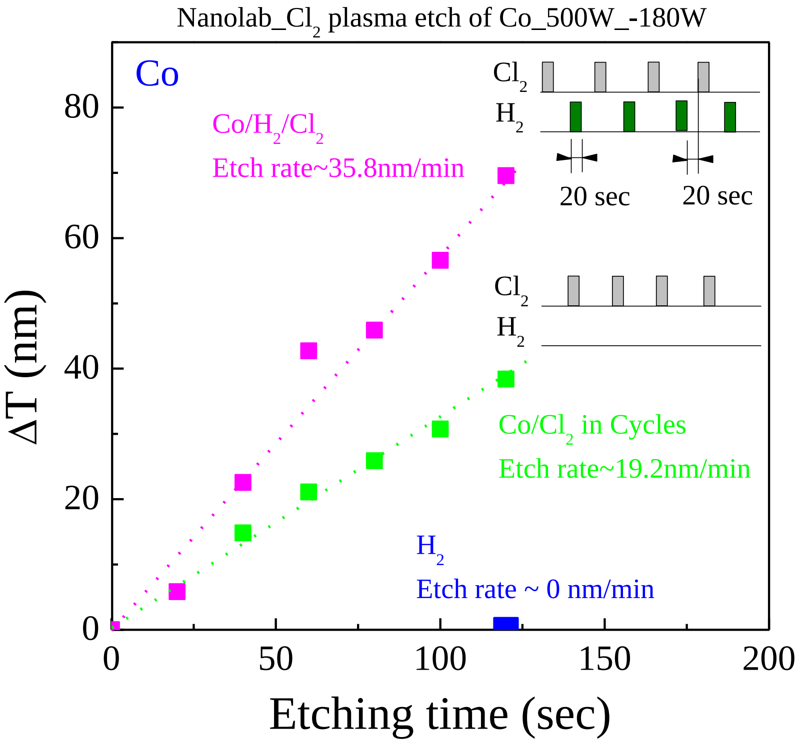
- **Based on volatility diagrams, the pressure of etch products, $CoCl_2$, $NiCl_2$ and $FeCl_3$, increases as increasing temperature**
- **The order of volatility: $FeCl_3$ > $CoCl_2$ > $NiCl_2$**

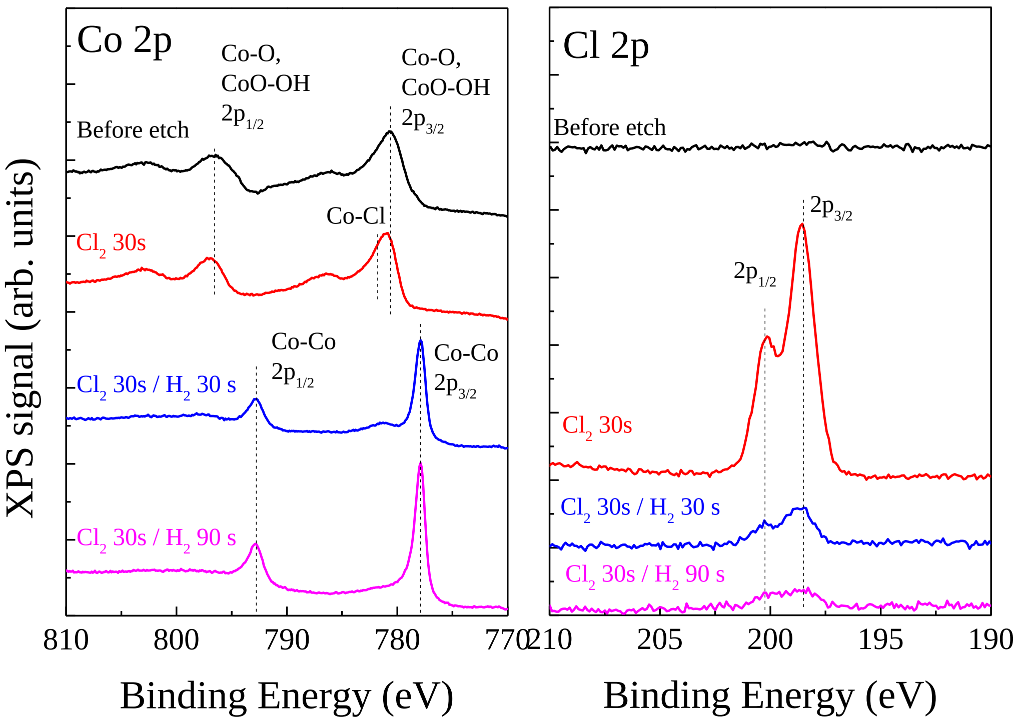
Evaluation of Sequential Chemistries



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

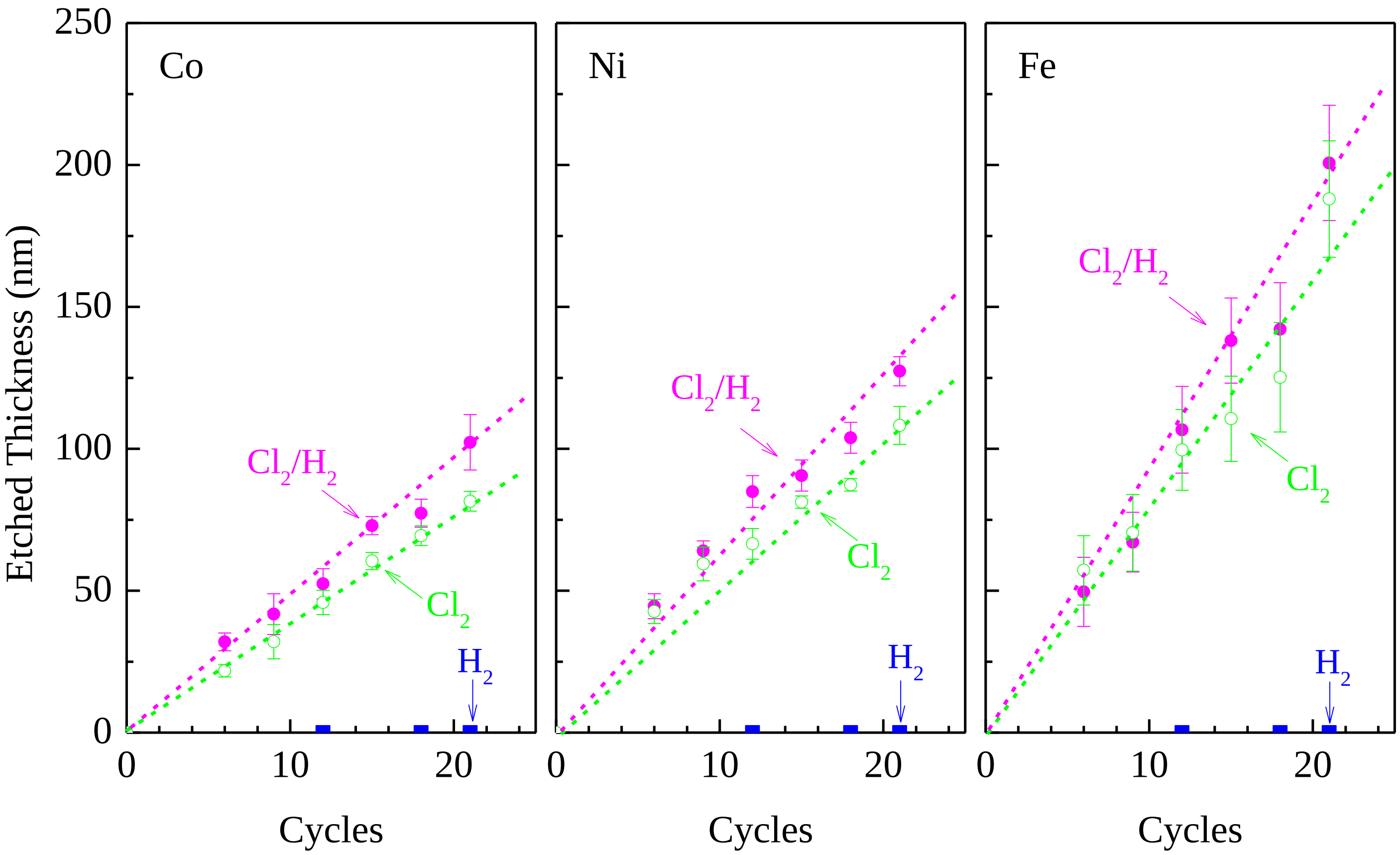
Co Etching by Cl_2/H_2





- **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**

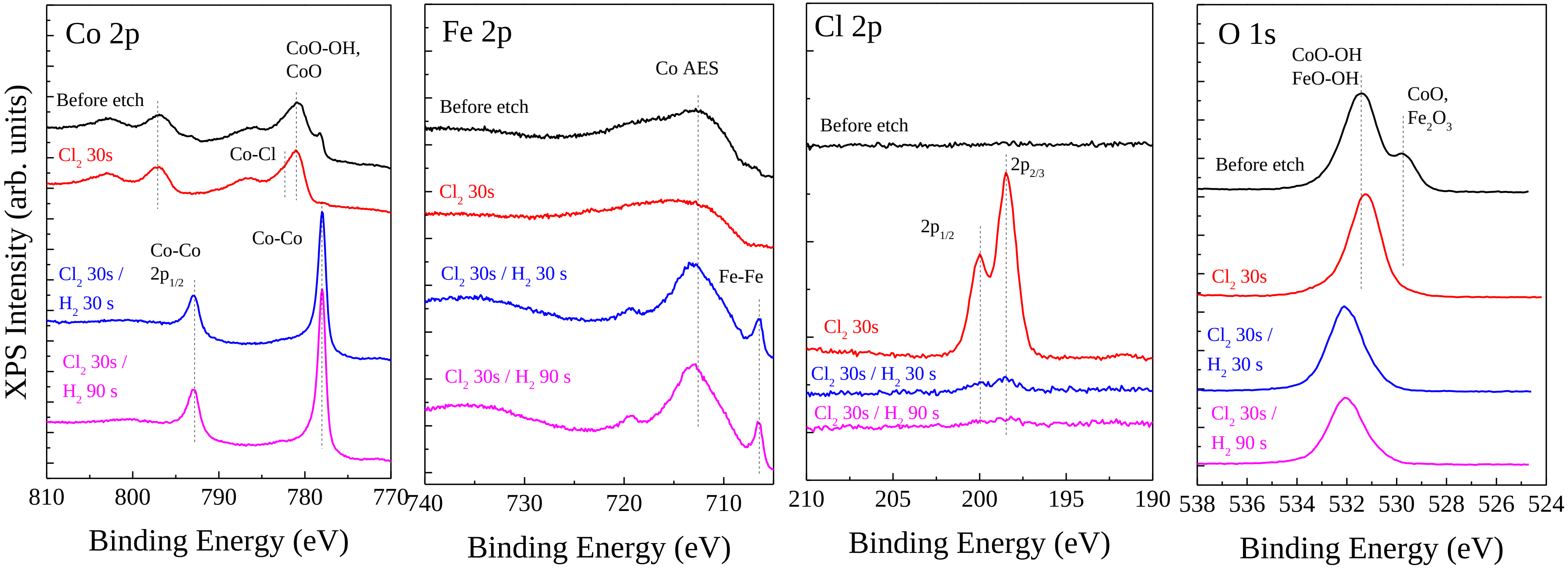
Co/Ni/Fe Etching by Cl_2/H_2



- 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

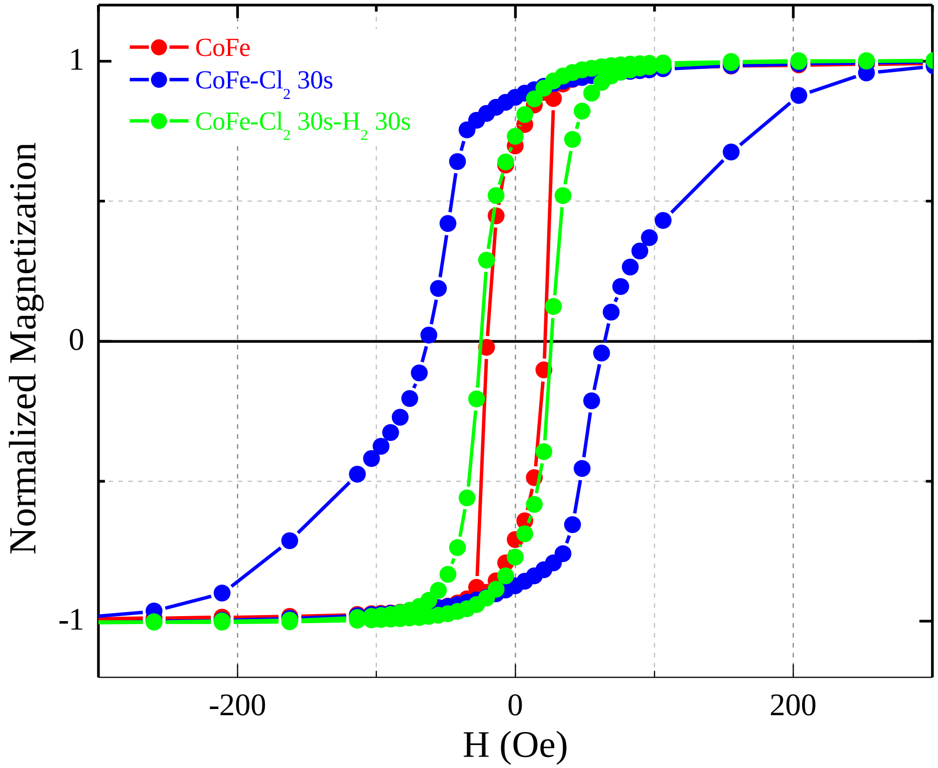
CoFe(1μm)



- **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**

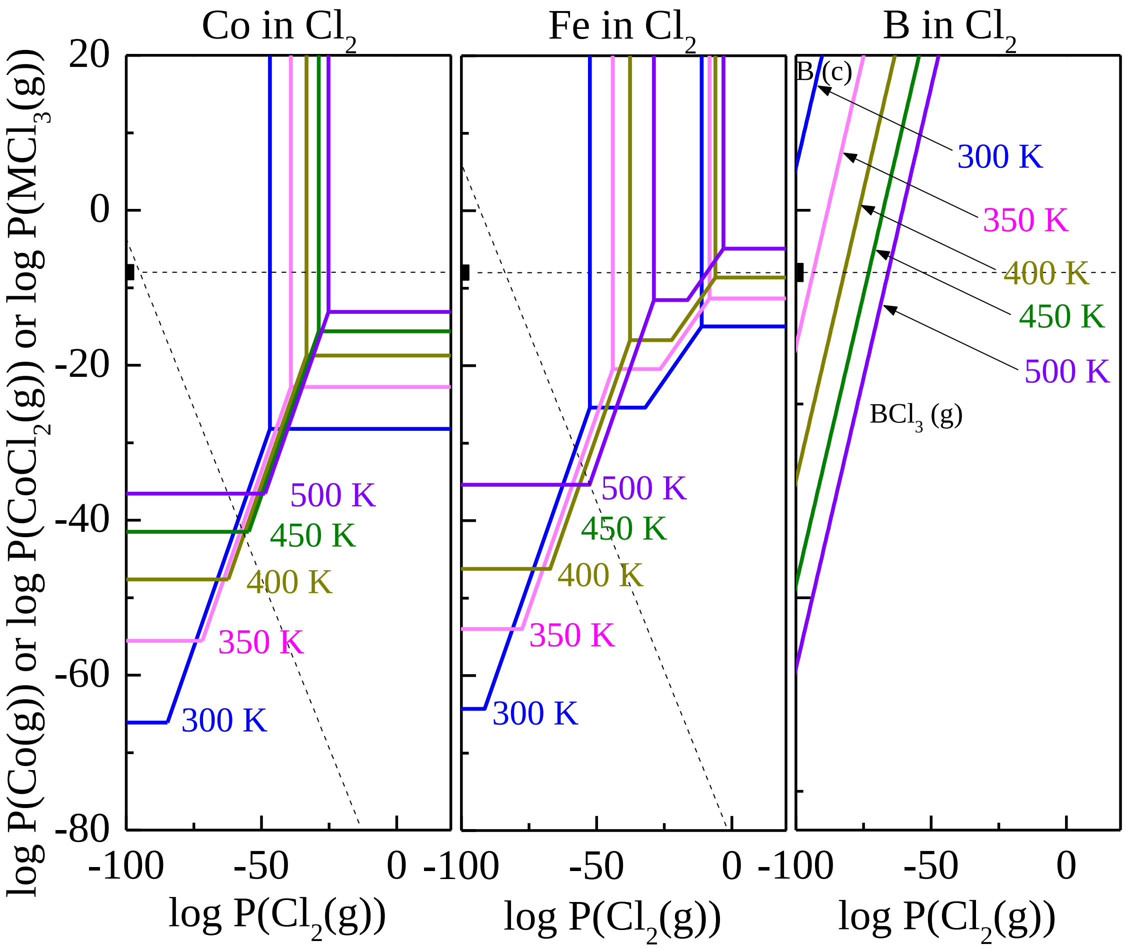
Magnetic Properties of CoFe (Cl_2-H_2)

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



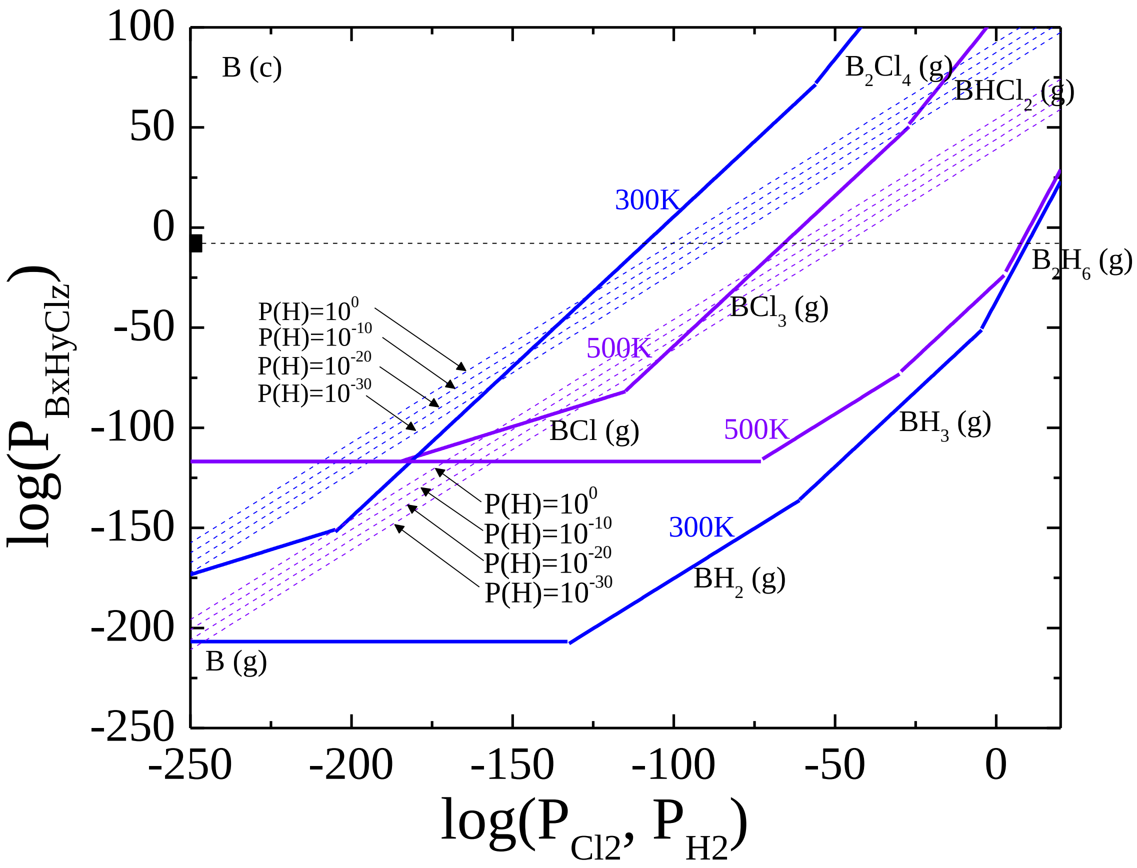
- **The degradation of magnetic property from Cl_2 plasma etch was restored by H_2 plasma treatment**

Thermodynamic Calculation of CoFeB



- **Formation of $BCl_{3(g)}$ can facilitate the removal of boron**

Thermodynamic Calculation of Boron

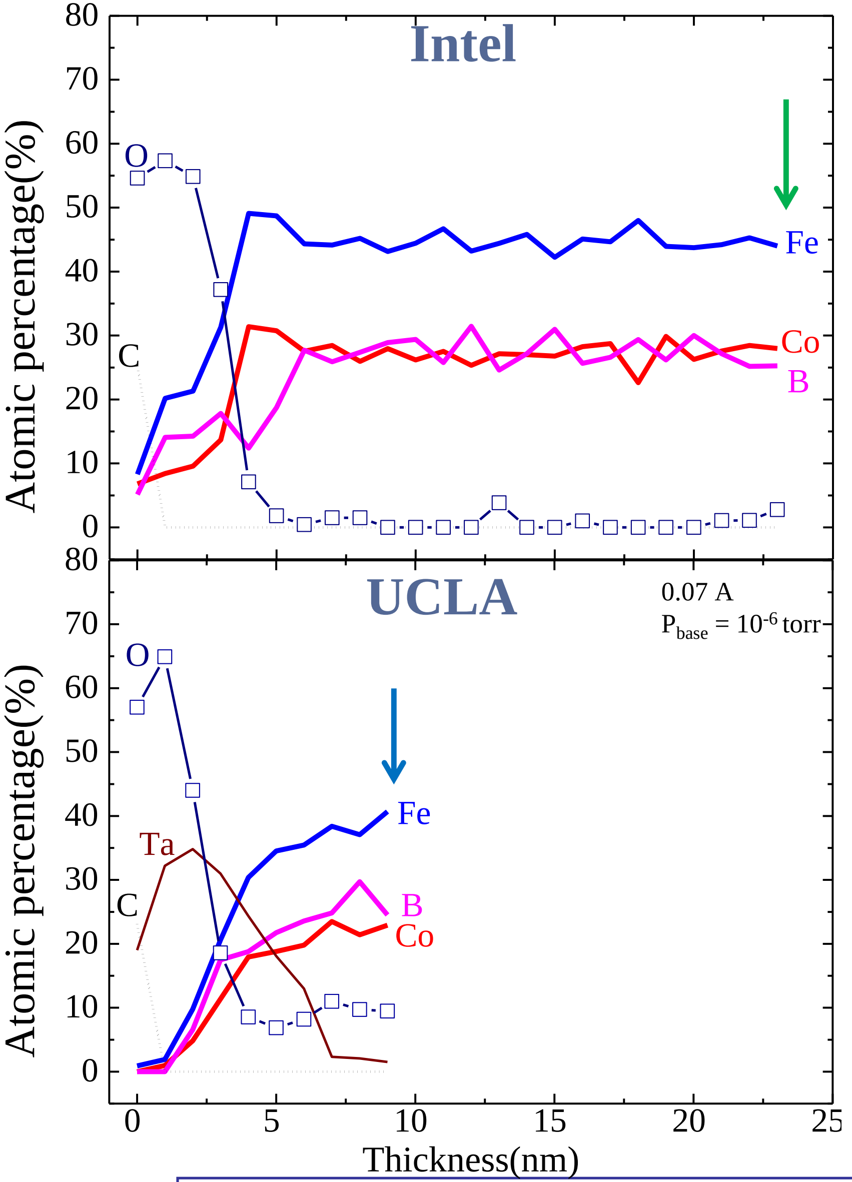


B-Cl_2 System	
B(g) – condensed phases equilibrium	
1	B(c) ↔ B(g)
BCl(g) - condensed phases equilibrium	
2	B(c) + 1/2 Cl_2(g)↔ BCl(g)
BCl_2(g) - condensed phases equilibrium	
3	B(c) + Cl_2(g) ↔ BCl_2(g)
BCl_3(g) – condensed phases equilibrium	
4	B(c) + 3/2 Cl_2(g) ↔ BCl_3(g)
B_2Cl_4(g) - condensed phases equilibrium	
5	2 B(c) + 2 Cl_2(g) ↔B_2Cl_4(g)

B-H_2 System	
BH_2(g) - condensed phases equilibrium	
6	B(c) + H_2(g) ↔ BH_2(g)
BH_3(g) – condensed phases equilibrium	
7	B(c) + 3/2 H_2(g) ↔ BH_3(g)
B_2H_6(g) - condensed phases equilibrium	
8	2 B(c) + 3 H_2(g) ↔ B_2H_6(g)

- **Volatility diagram predicts formation of volatile BCl_3(g) and B_2Cl_4(g) species at very low pressures of Cl_2**
- **B forms volatile species with H at much higher pressures**

Surface Oxidation of CoFeB

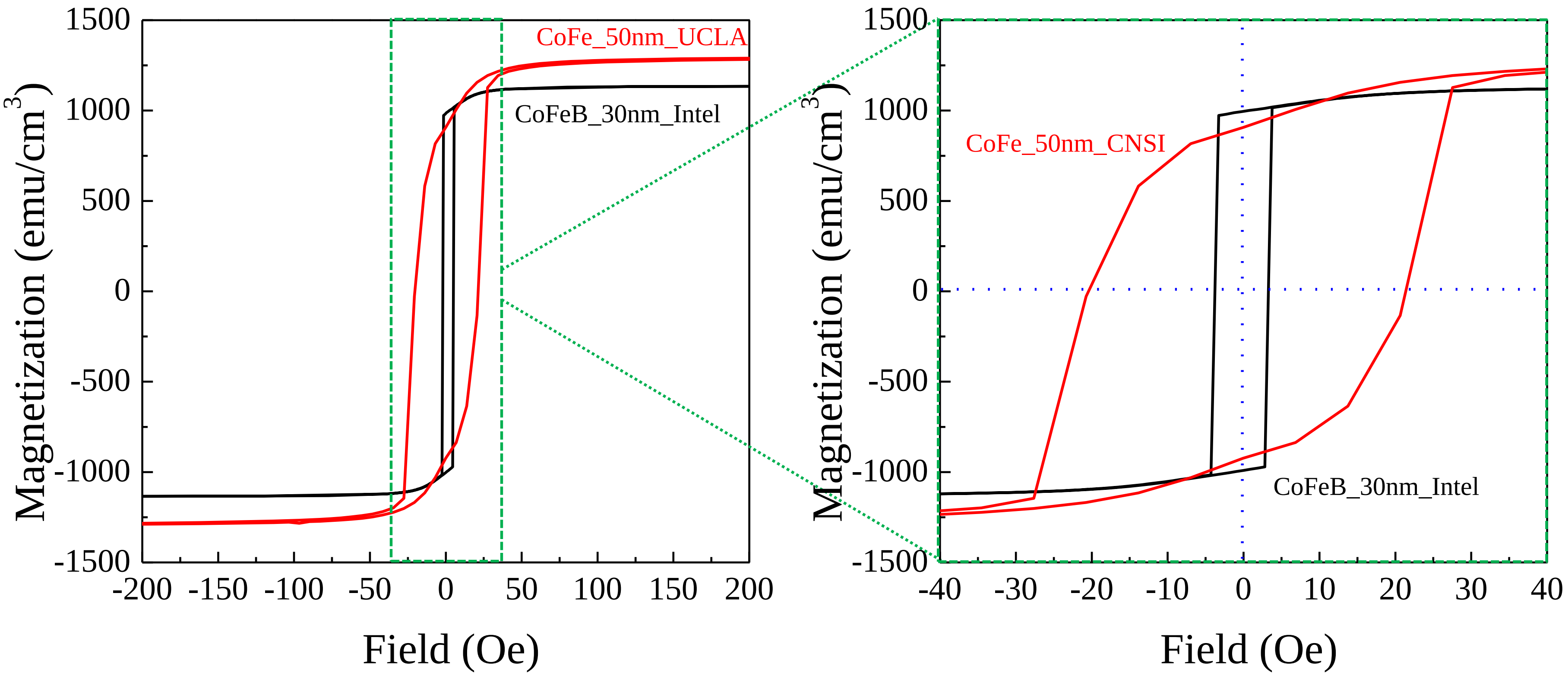


Final: $Co_{29}Fe_{45}B_{26}$
Target (not disclosed)
Elemental: $Co_{28}Fe_{44}B_{25}O_3$

Final: $Co_{27}Fe_{45}B_{28}$
Target: $Co_{20}Fe_{60}B_{20}$
Elemental: $Co_{23}Fe_{41}B_{26}O_{10}$

- **Difficulty in using "in-house" deposited CoFeB film for etch studies due to Ta capping layer**
- **Continue on to investigate etch chemistries for CoFeB with Intel film**

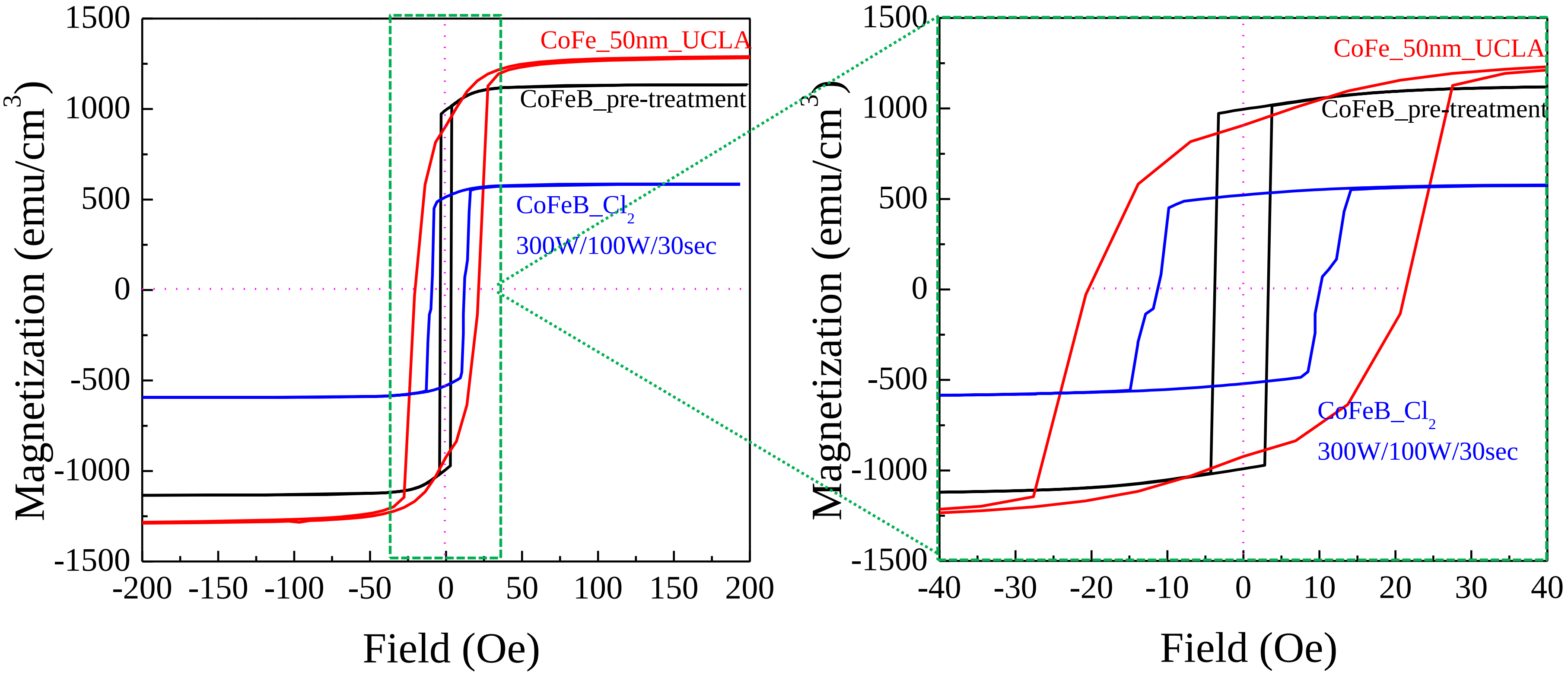
SQUID of CoFe and CoFeB



- **Since the doping of B disrupts the crystallinity of CoFe, the coercivity and saturated magnetization decreased**
- **Coercivity of blank CoFeB (30nm) from Intel is about 3.5Oe which is much smaller than that of CoFe (50nm)**

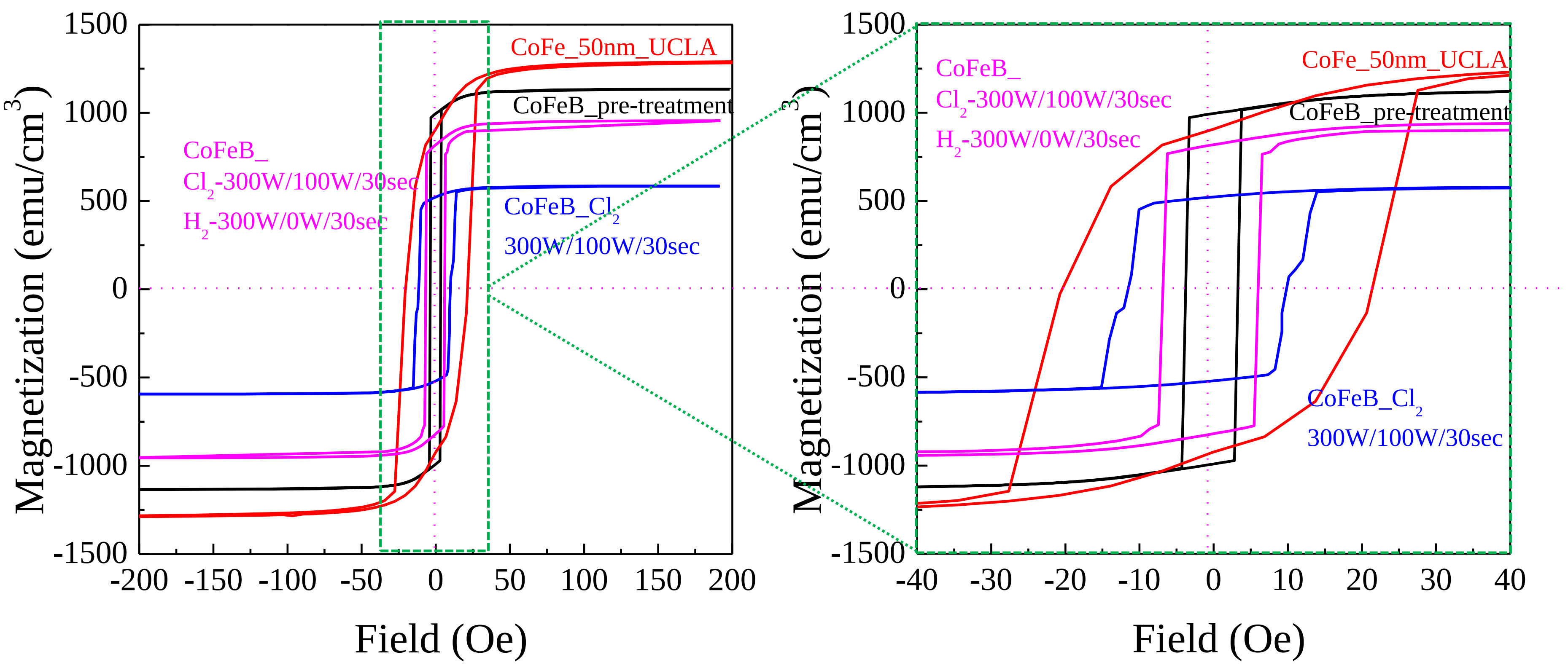
	Coercivity	Ms
CoFe	20.0 Oe	1300
CoFeB	3.5 Oe	1134

SQUID after CoFeB w/ Cl_2 30sec



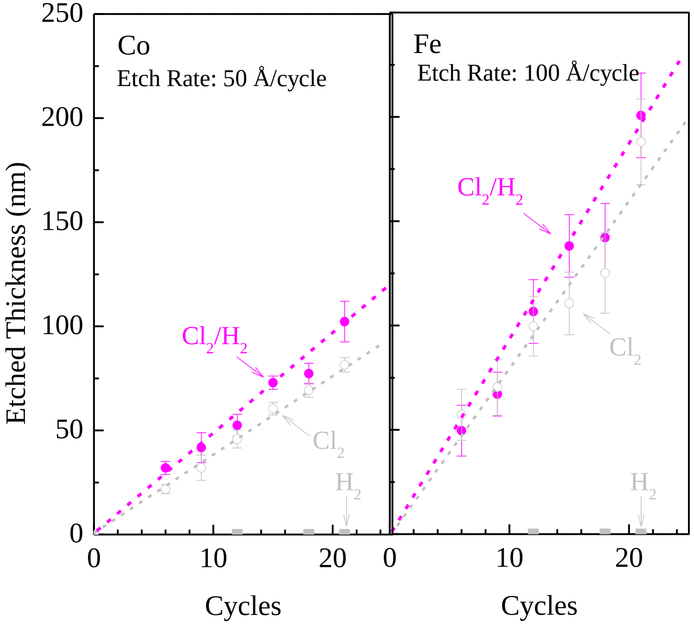
- **30 s exposure to Cl_2 plasma results in formation of metal and boron chloride species, increasing coercivity**

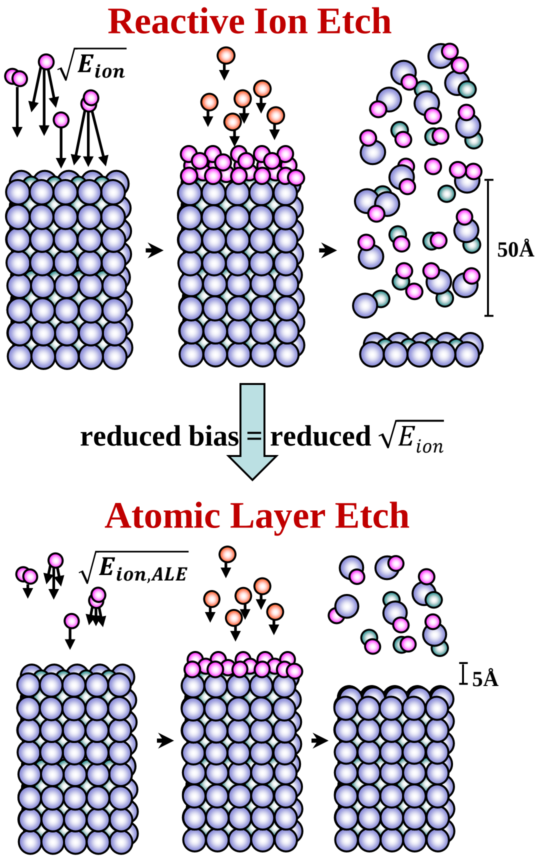
SQUID after CoFeB Cl_2/H_2



- **Subsequent exposure to H_2 plasma removes chlorides, partially restoring magnetic behavior**
- **Need to further investigate plasma parameters and sequence exposure times**

Pathway towards Atomic Layer Etch





$ER = f(\sqrt{E_{ion}})$	Co	Fe
Measured ER	50 Å/cyc	100 Å/cyc
Target ER	5 Å/cyc	5 Å/cyc
ER reduction	0.1	0.05
E_{ion} reduction	0.01	0.0025

For ALE of Co

$$ER = \alpha\sqrt{E_{ion}}$$

$$\Downarrow$$

$$\frac{ER}{ER_{ALE}} = \frac{\sqrt{E_{ion}}}{\sqrt{E_{ion,ALE}}}$$

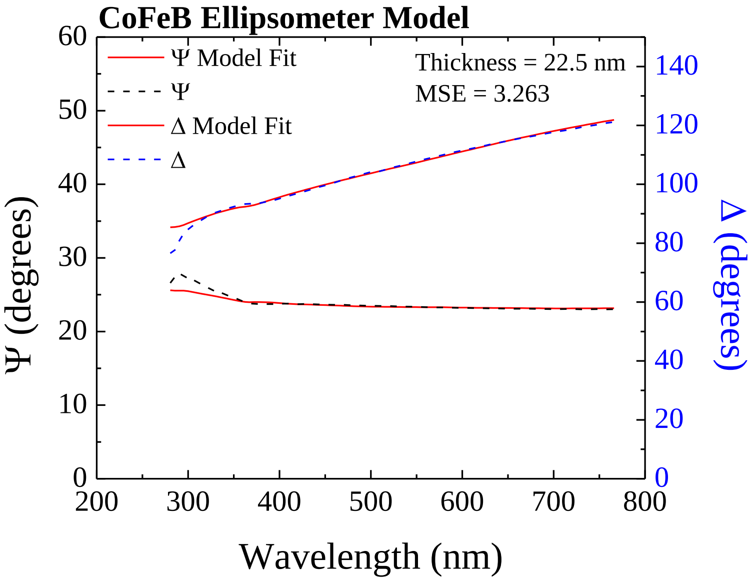
$$\Downarrow$$

$$E_{ion,ALE} = \left(\frac{ER}{ER_{ALE}}\right)^2 E_{ion} = \frac{E_{ion}}{100}$$

- **Control surface chlorination by reducing ion energy**
- **The use of ion beams might be beneficial to control the ion energy**

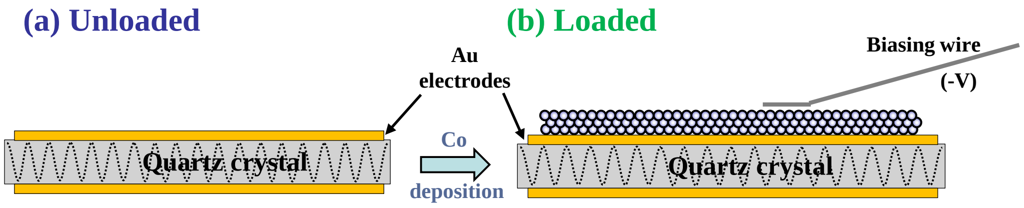
Quantification of ALE

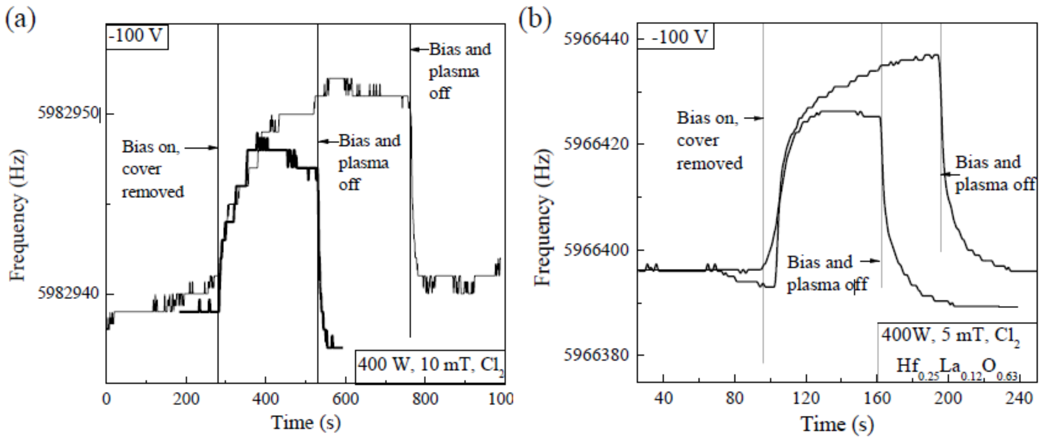
Ellipsometry
(in-situ)



- Ineffective on reflective materials (CoFeB)
- Heavily dependent on degree of surface roughness

QCM
(in-situ)





- Difficult to bias substrate due to sample holder
- Use ion beams or ions extracted from a plasma to control the ion energy

- Ex-situ, e.g. SEM, only captures large thickness change over many cycles
- In-situ can record instantaneous etch and deposition steps during each cycle

Reference

[1] K. Kinoshita et al. Jpn. J. Appl. Phys. 51 (2012) 08HA01.
[2] Kinoshita et al. Jpn. J. Appl. Phys. 49 (2010) 08JB02-6.
[3] J. Zhang, et al., JAP 107 (2010) 09A318.
[4] J. M. Slaughter, Annu. Rev. Mater. Res., 39: 277-96, (2000).
[5] S.D. Athavale, D.J. Economou, JVST A, 13, 966-971 (1995).
[6] A. Agarwal, M.J. Kushner, JVST A, 27, 37 (2009).
[7] D. Metzler, *et al.*, JVST A, 32, 020603 (2014).

Industrial Interactions and Technology Transfer

- **Conference call with Intel, June 12, 2014 (Satyarth Suri)**
- **Conference call with Intel, July 9, 2014 (Satyarth Suri)**
- **Conference call with Intel, August 14, 2014 (Satyarth Suri)**
- **Conference call with Intel, September 11, 2014 (Satyarth Suri)**
- **Conference call with Intel, October 30, 2014 (Satyarth Suri)**
- **Conference call with Intel, December 18, 2014 (Satyarth Suri)**
- **Conference call with Intel, February 19, 2015 (Satyarth Suri)**

Future Plans

Next Year Plans

- Improve CoFeB etch by investigating bulky organic ligands which generate high volatile etch products
- Identification of suitable chemistries to provide volatile etch products for hard-to-etch materials

Long-Term Plans

- Formulate models to predict etch product from plasma processes
- Suggest viable plasma chemistries for atomic layer etch of metal alloy films

Publications, Presentations, and Recognitions/Awards

Presentation:

- **Contributed talk at AVS International Symposium, November 2014**
  (J.K. Chen, N. Altieri, M. Paine, and J.P. Chang, “Non-PFC Plasma Chemistries for Patterning Low-k Dielectric Materials”)

Publication:

- **“Thermodynamic assessment and experimental verification of reactive ion etching of magnetic metal elements”, June 2014**
- **“Viable chemical approach for patterning nanoscale magnetoresistive random access memory”, January 2015**
- **Deliverable Report, P065582, “Non-PFC Plasma Chemistries for Patterning Complex Materials/Structures”, January 2014**