Alternative Etchants for Atomic Layer Etch of Magnetic Materials

(*Task Number: 425.046*)

PIs:

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Graduate Students:

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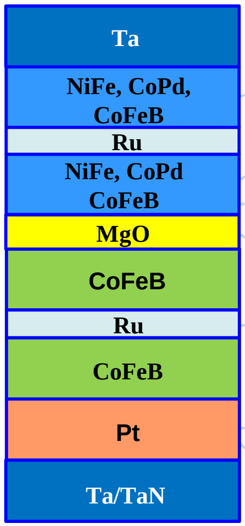
- **Nicholas Altieri, PhD student, Chemical and Biomolecular Engineering, UCLA**

Objectives

- **Assess the feasibility of chemistries in patterning magnetic materials**
- **Screen viable chemistries in patterning magnetic materials by thermodynamic analysis**
- **Verify the thermodynamic calculation by performing the plasma etching experiments**
- **Advance towards atomic layer etch of magnetic thin films**

Challenges in Patterning Magnetic Metal



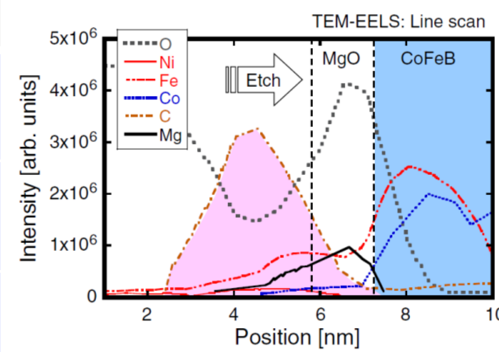
Potential chemistry for MRAM materials

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



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

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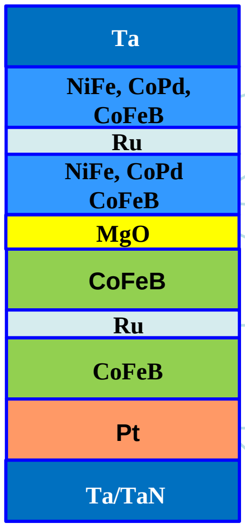
[1] K. Kinoshita et al. Jpn. J. Appl. Phys. 51 (2012) 08HA01, [2] Kinoshita et al. JJAP 49 (2010) 08JB02-6, [3] J. Zhang, et al., JAP 107 (2010) 09A318

Challenges in Patterning Magnetic Metal



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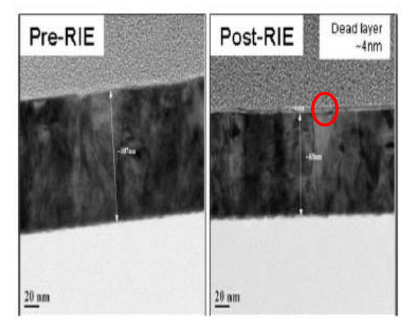

Dead layer formation inducing magnetic property degradation after Cl_2 plasma [5]

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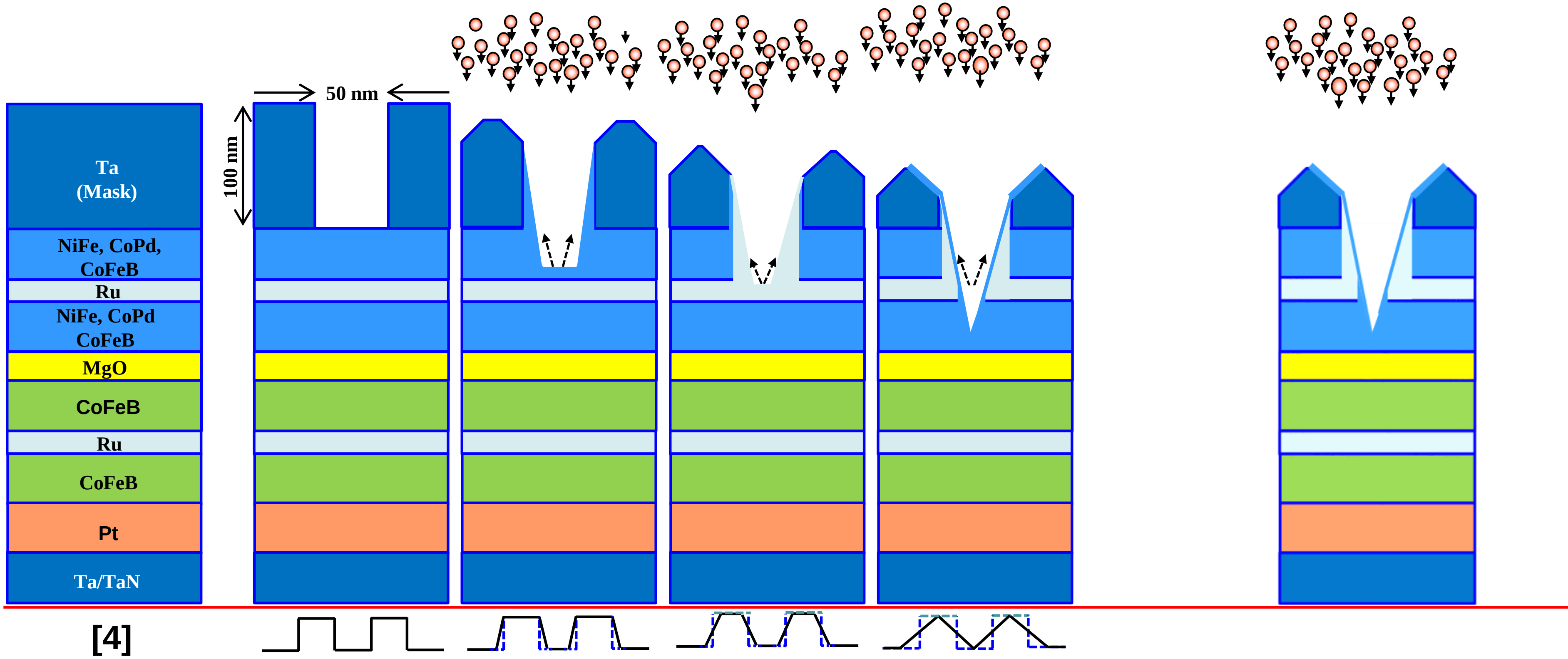
[1] K. Kinoshita et al. Jpn. J. Appl. Phys. 51 (2012) 08HA01, [2] Kinoshita et al. JJAP 49 (2010) 08JB02-6, [3] J. Zhang, et al., JAP 107 (2010) 09A318

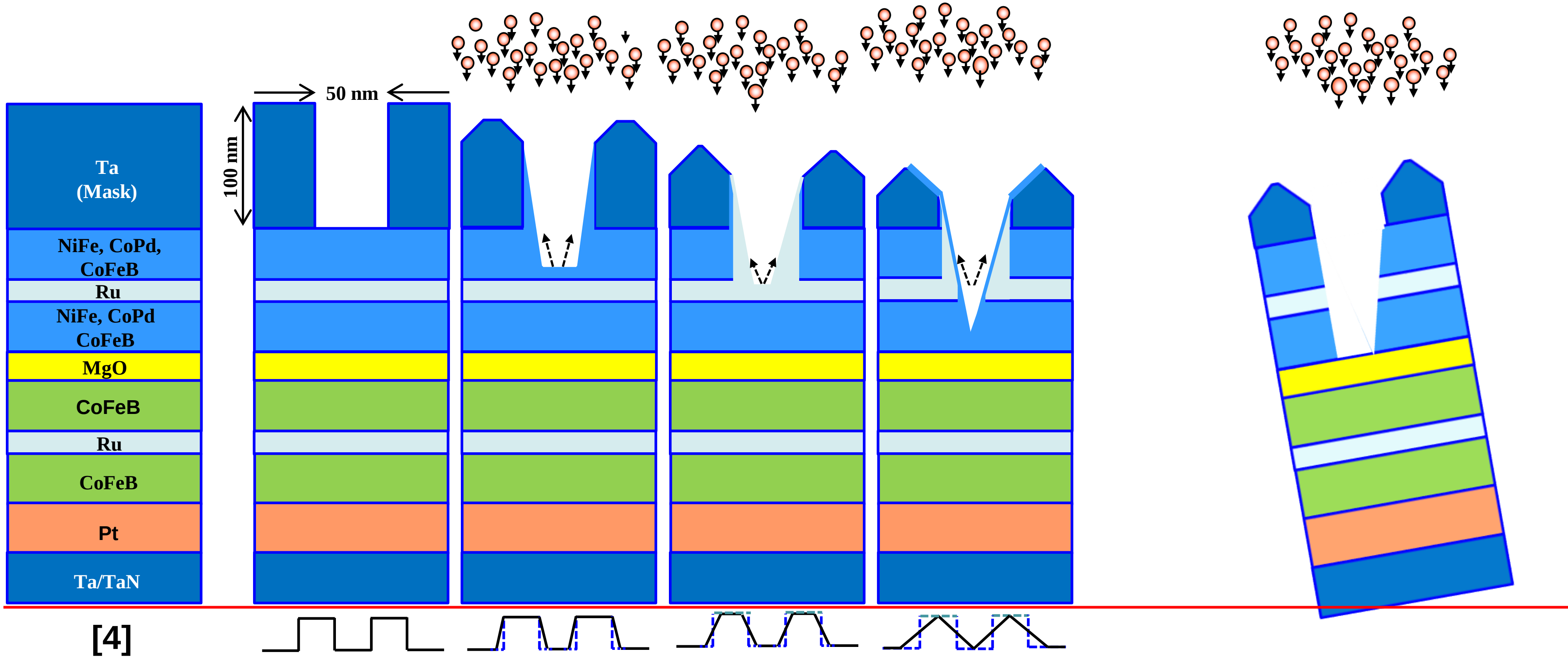
Sidewall Re-deposition



- 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)

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

Sidewall Re-deposition



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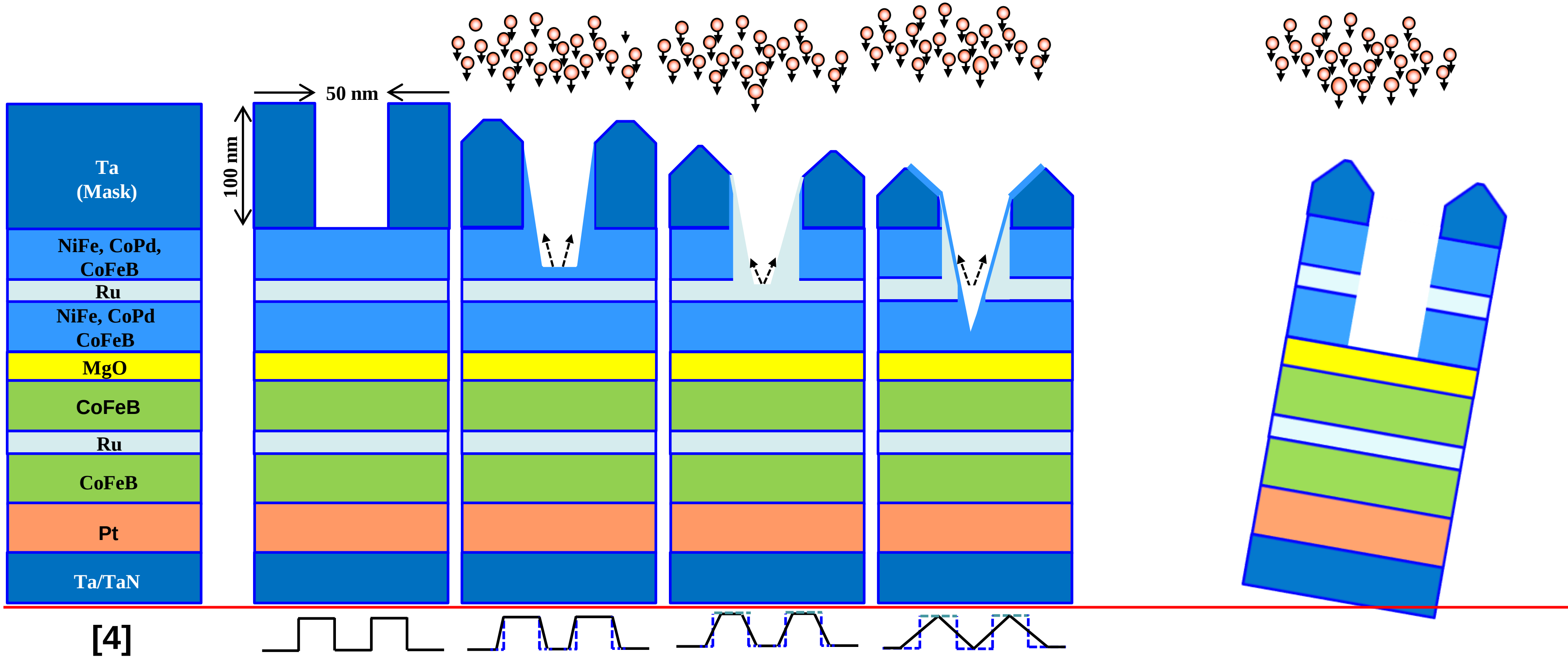

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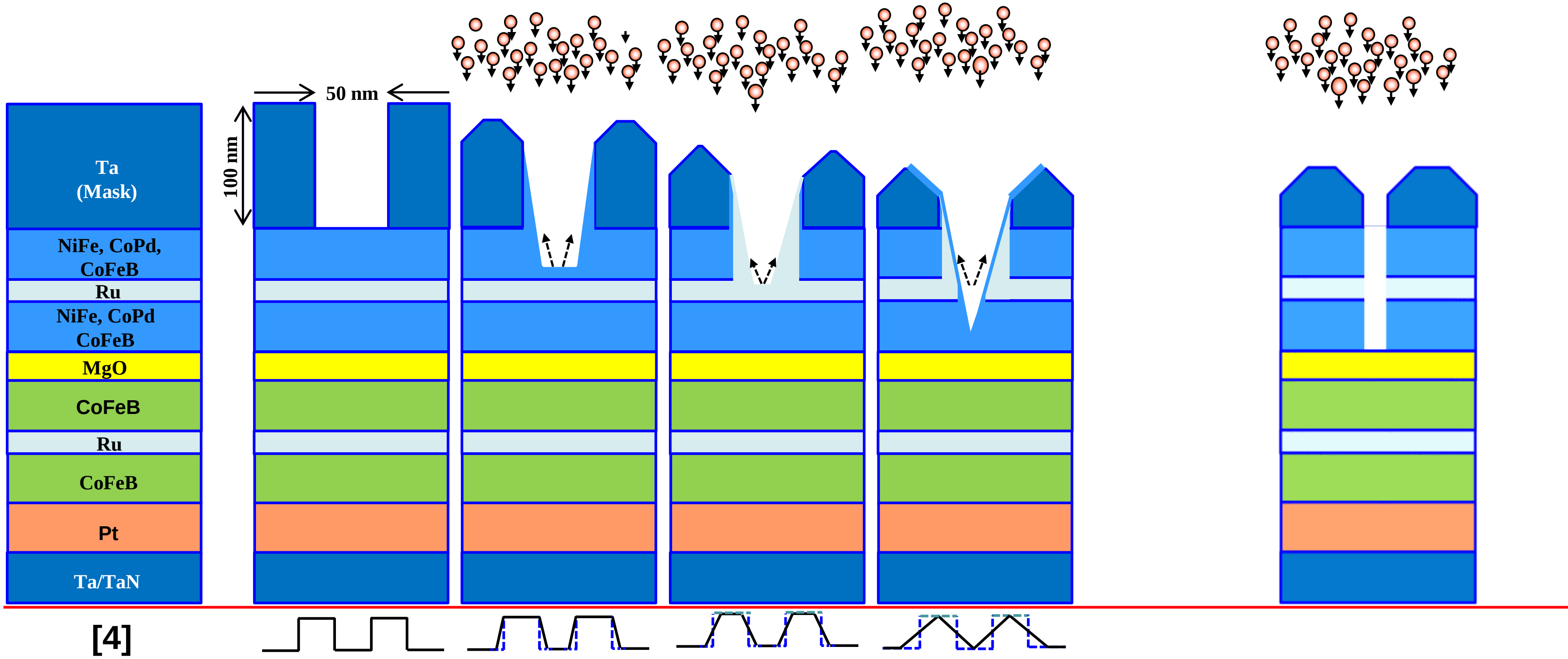

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Target of MRAM Metal Etch

2014 Specified Metrics

Intel specified metrics:

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:

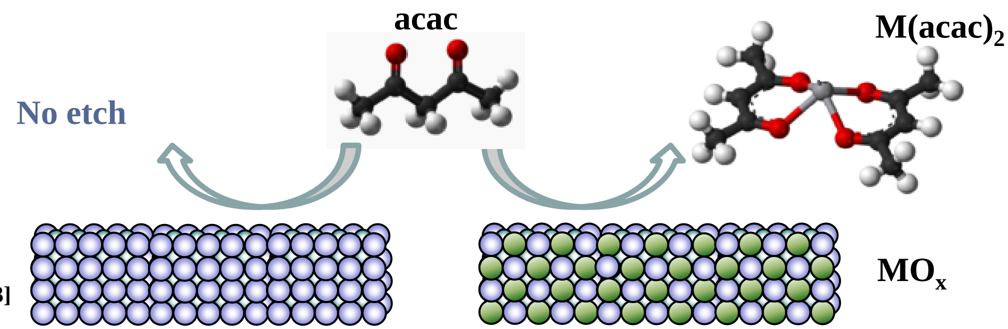
1	Co-based, Pt, and Cu metallic films
2	Advancement towards atomic layer etch of hard-to-pattern materials
3	Viability of halide chemistry? →Volatility analysis

Priority of research:

CoFeB → Pt → Cu

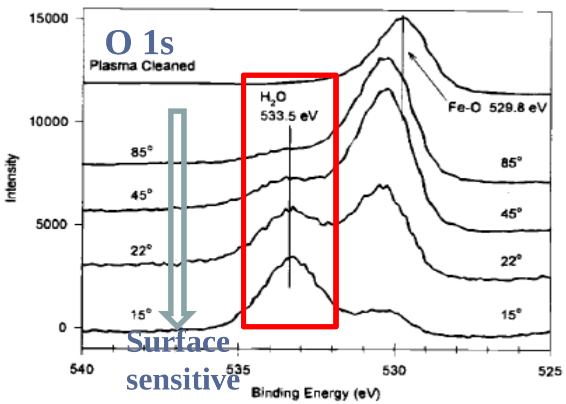
Effect of Surface States

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



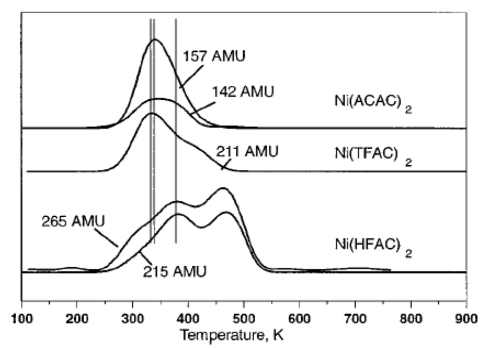
M : Fe[1], Ni[2], Cu[3]

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

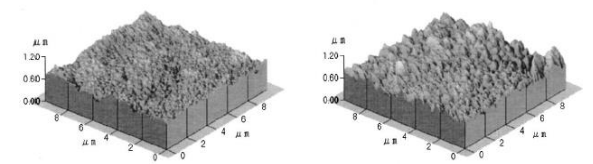


[8] Ni$(acac)_2$, Ni$(tfac)_2$, and Ni$(hfac)_2$

Acac / Ni , TPD, Ts = 100 K



[9] Roughness change of CuO$_x$ film



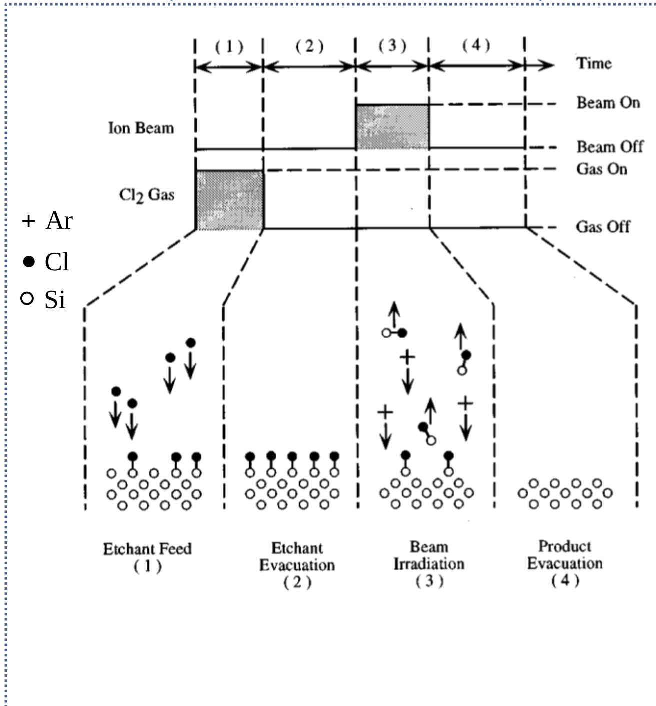
Before Hfac
RMS roughness :
50 nm

After Hfac
RMS roughness :
90 nm

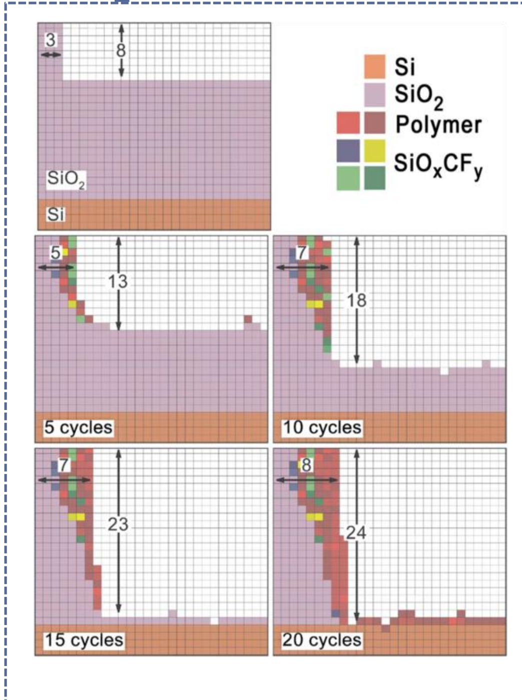
[7] D. W. Hess et al ECS 142 (1995) 961 ; [8] R. I. Masel et al. JVST A. 16 (1998) 3259; [9] S.W. Kang et al. JVST B. 17 (1999) 154

Atomic Layer Etch (ALE)

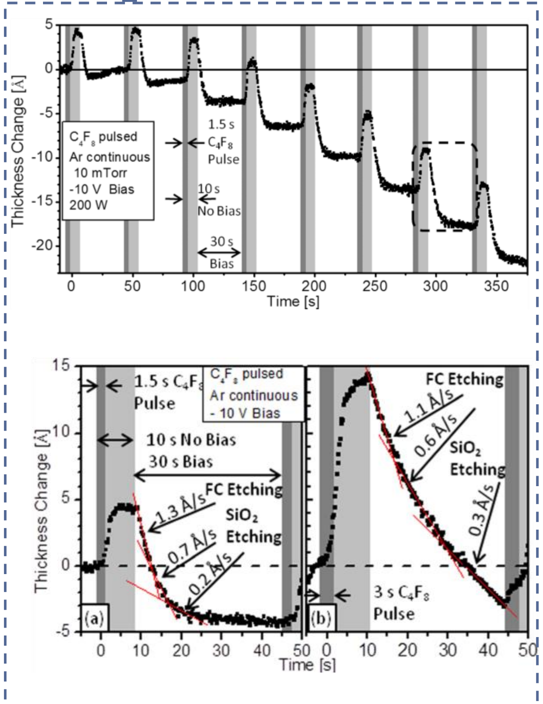
Si (Economou 1995)



SiO_2 (Kushner 2004)



SiO_2 (Oehrlein 2014)

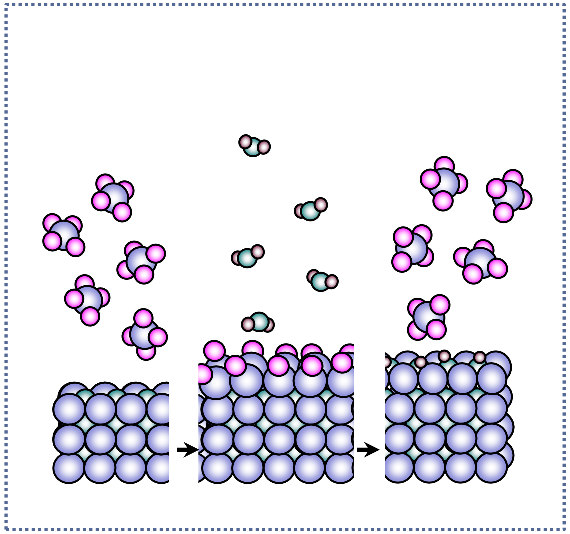


- **Atomic layer etch of Si (1995) achieved through sequence of monolayer chlorination and Ar^+ bombardment**
- **ALE of SiO_2 simulated (2004) and confirmed experimentally by pulsed C_4F_8 with continuous Ar irradiation (2014)**

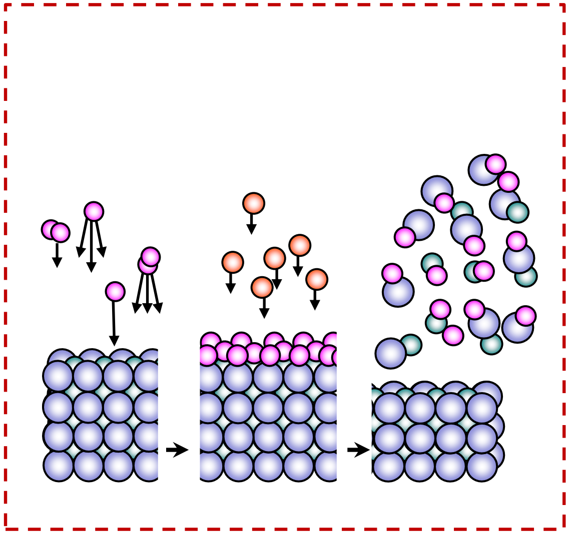
[5] S.D. Athavale, D.J. Economou, JVST A, 13, 966-971 (1995), [6] A. Agarwal, M.J. Kushner, JVST A, 27, 37 (2009), [7] D. Metzler, *et al.*, JVST A, 32, 020603 (2014).

Strategy for ALE

ALD



ALE



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

- **Self limiting nature of ALD process comes from reaction and subsequent regeneration of surface species**
- **Current strategy is to reverse ALD, requiring only one 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 CoFeB and Pt

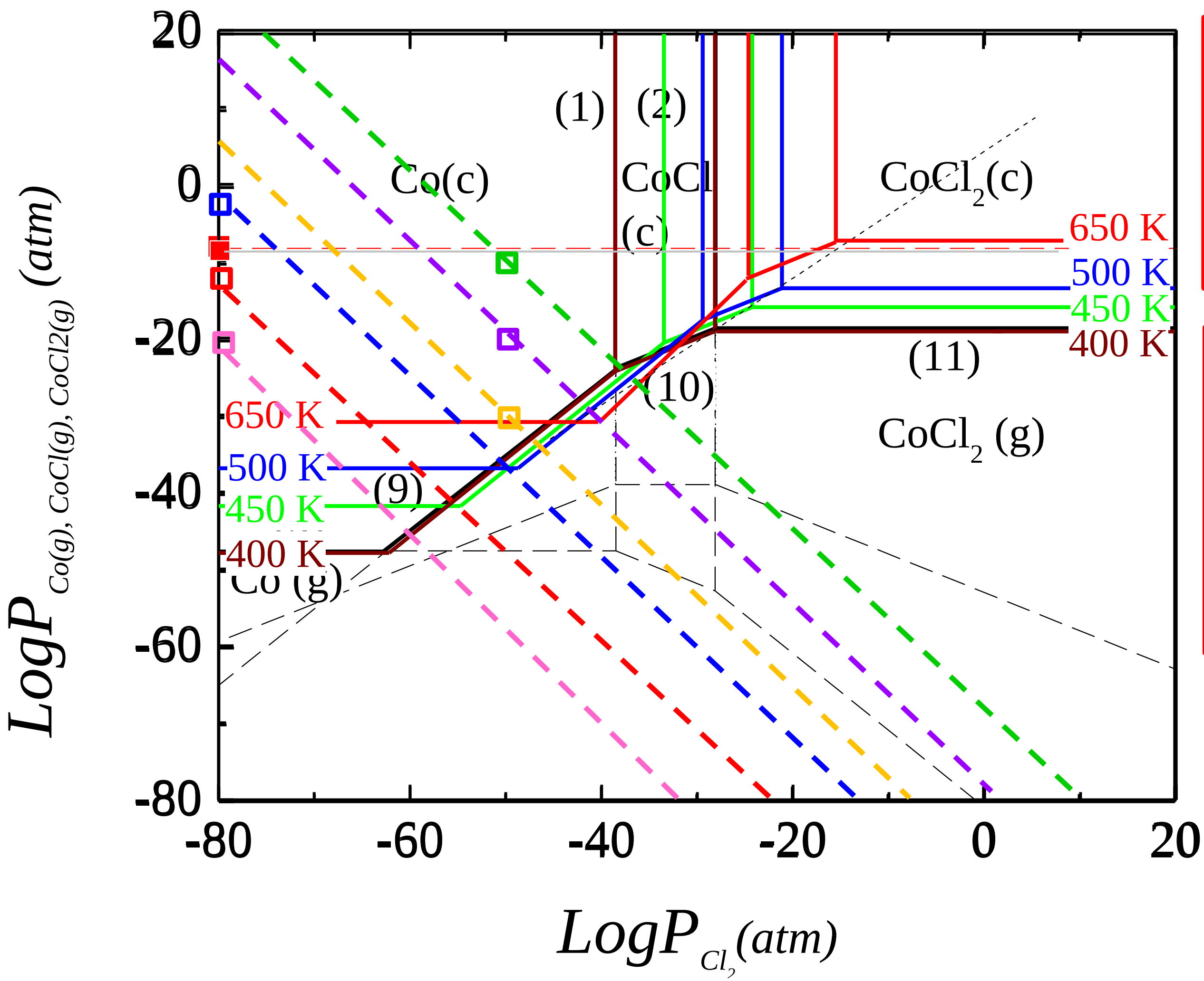
Surface analysis using XPS

- 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	$CoCl_2(c) \leftrightarrow CoCl_2(g)$

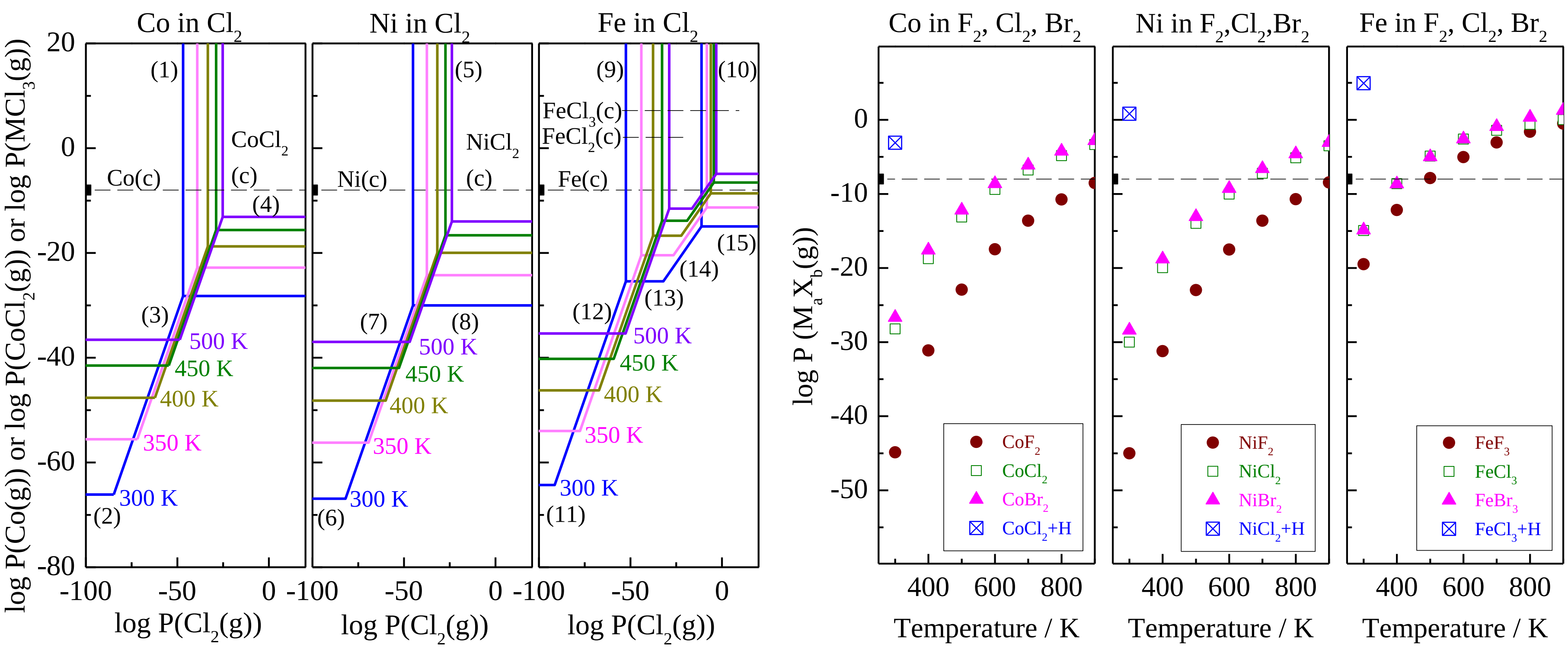
$CoCl_2(c) + O(g) \rightarrow CoO(g) + Cl_2(g)$

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

$CoCl_2(c) + H(g) \rightarrow CoH(g) + Cl_2(g)$

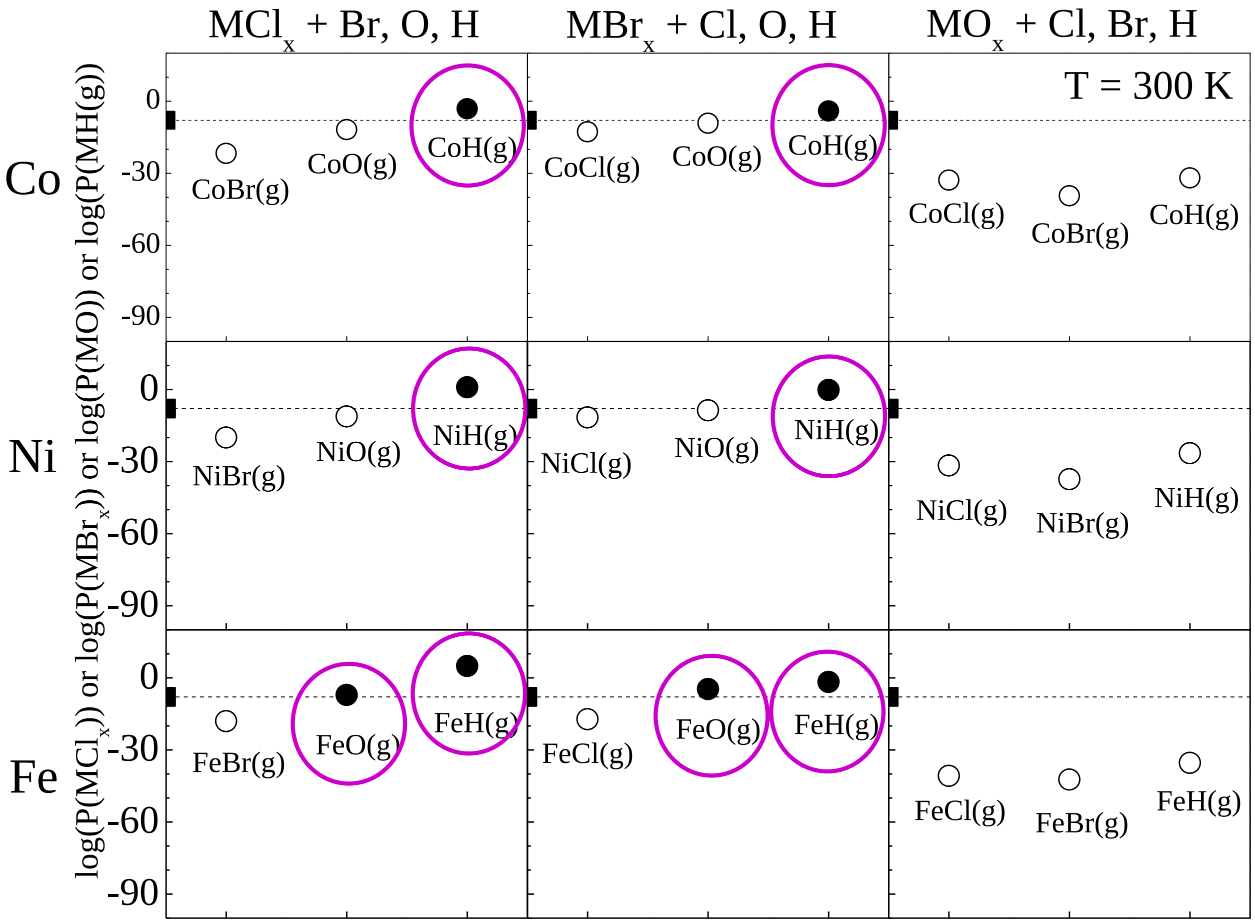
$CoCl_2(c) + 3H(g) \rightarrow CoH(g) + 2HCl(g)$

Volatility Diagram of Co/Ni/Fe-Cl_2



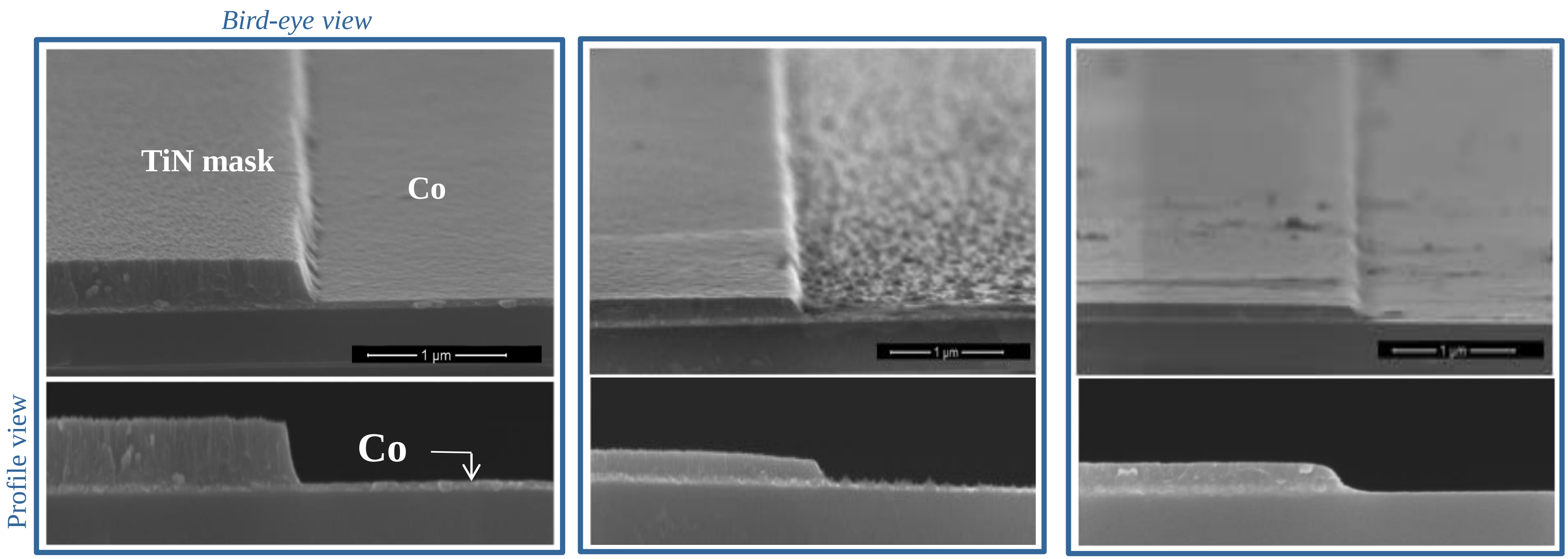
- **Based on volatility diagrams, the pressure of etch products, $CoCl_2$, $NiCl_2$ and $FeCl_3$, increases as increasing temperature**
- **The order of volatility: $FeCl_3$ > $CoCl_2$ > $NiCl_2$**

Evaluation of Sequential Chemistries



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

Co Etching by Cl_2/H_2



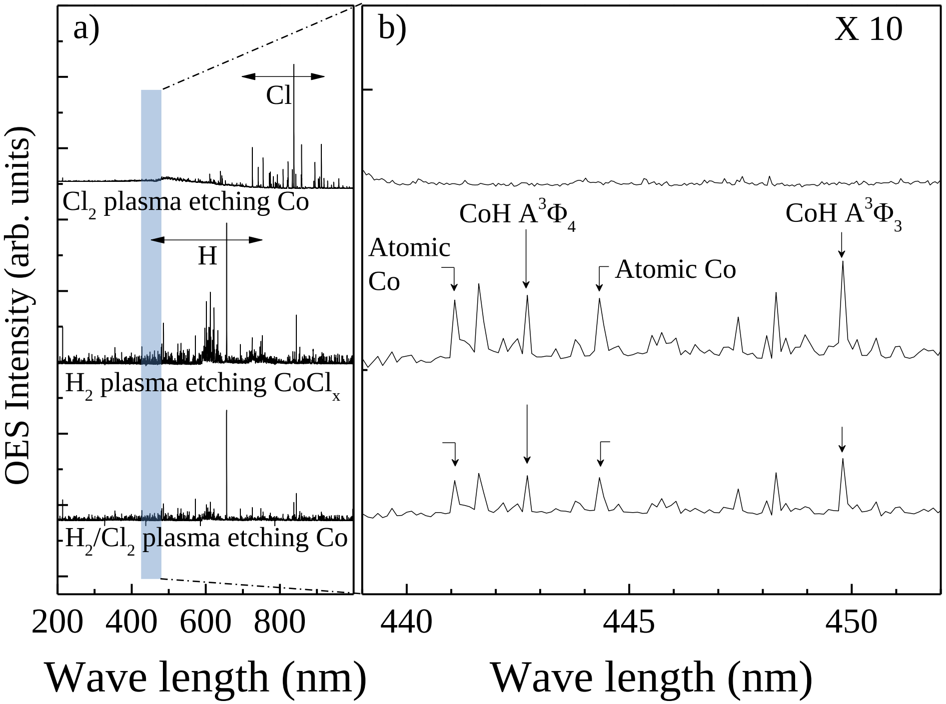
Before etch (Co= 50 nm) | Cl_2 plasma exposure | H_2 plasma exposure

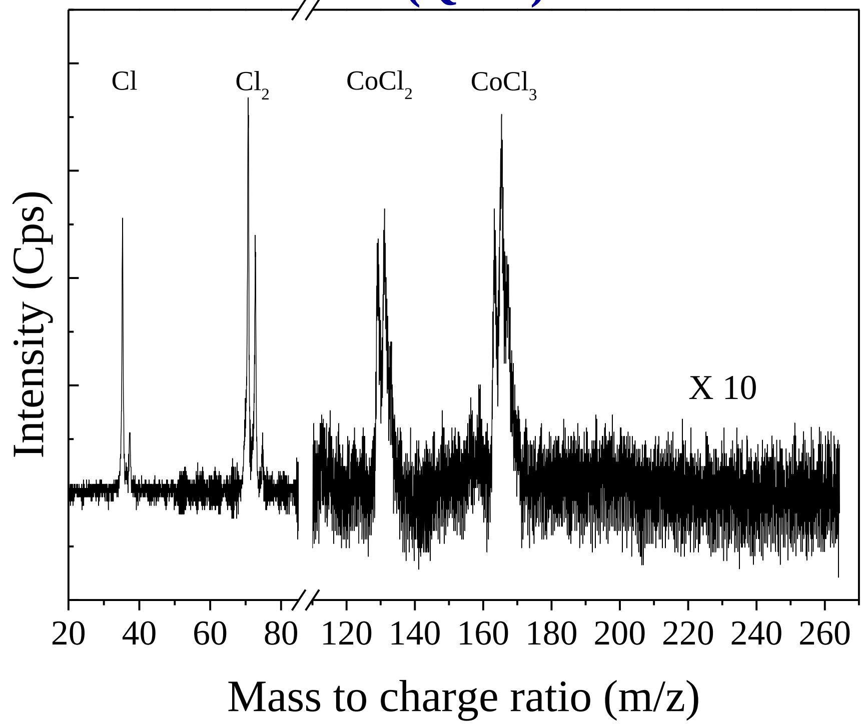
- **SEM images for sequential plasma show surface roughness after Cl_2 exposure**
- **Film was visibly clean following treatment with hydrogen plasma**

Co Etching by Cl_2/H_2

Optical Emission Spectra (OES)

Quadrupole Mass Spec (QMS)

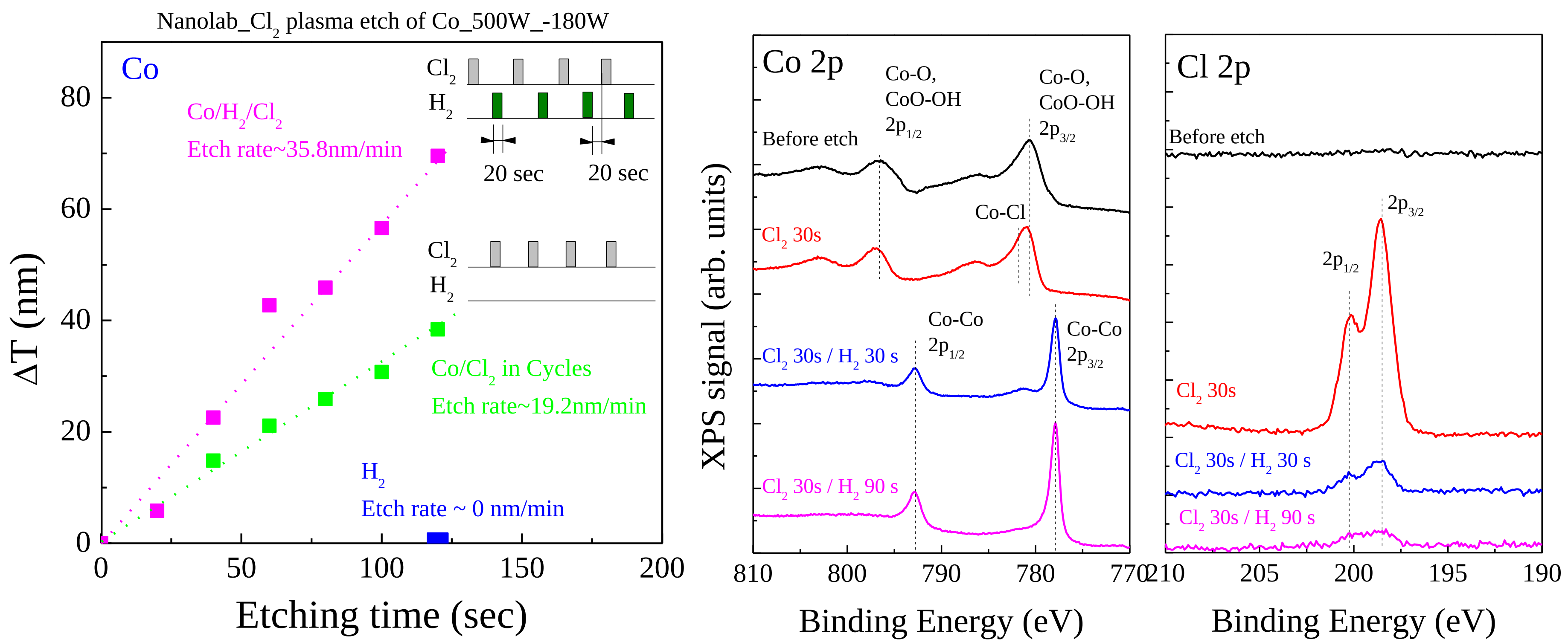




- **OES confirmed CoH wformation hen hydrogen plasma reacted with chlorinated Co**
- **QMS spectrum confirmed the formation of both $CoCl_2$ and $CoCl_3$**

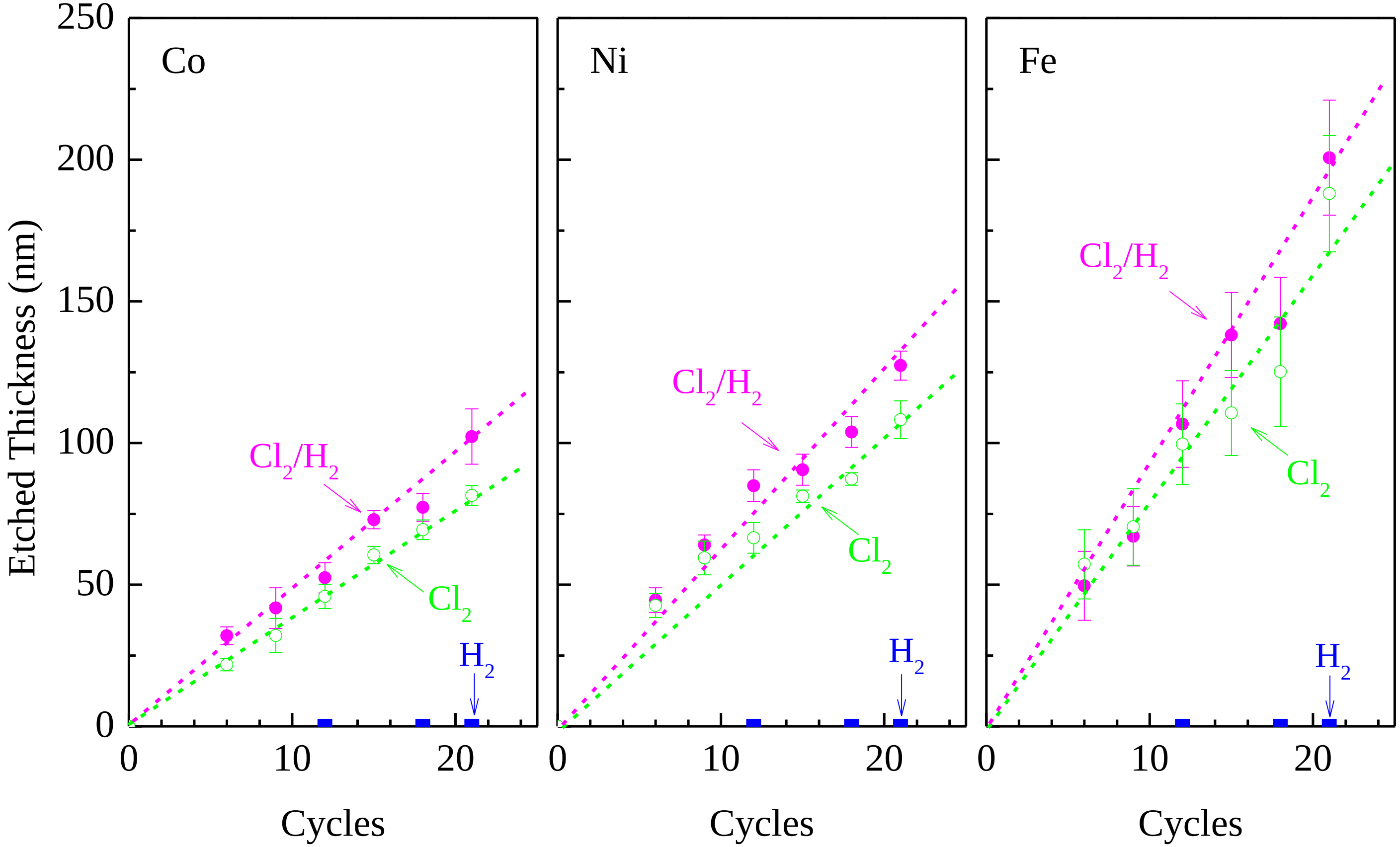
Chang Lab UCLA

Co Etching by Cl_2/H_2



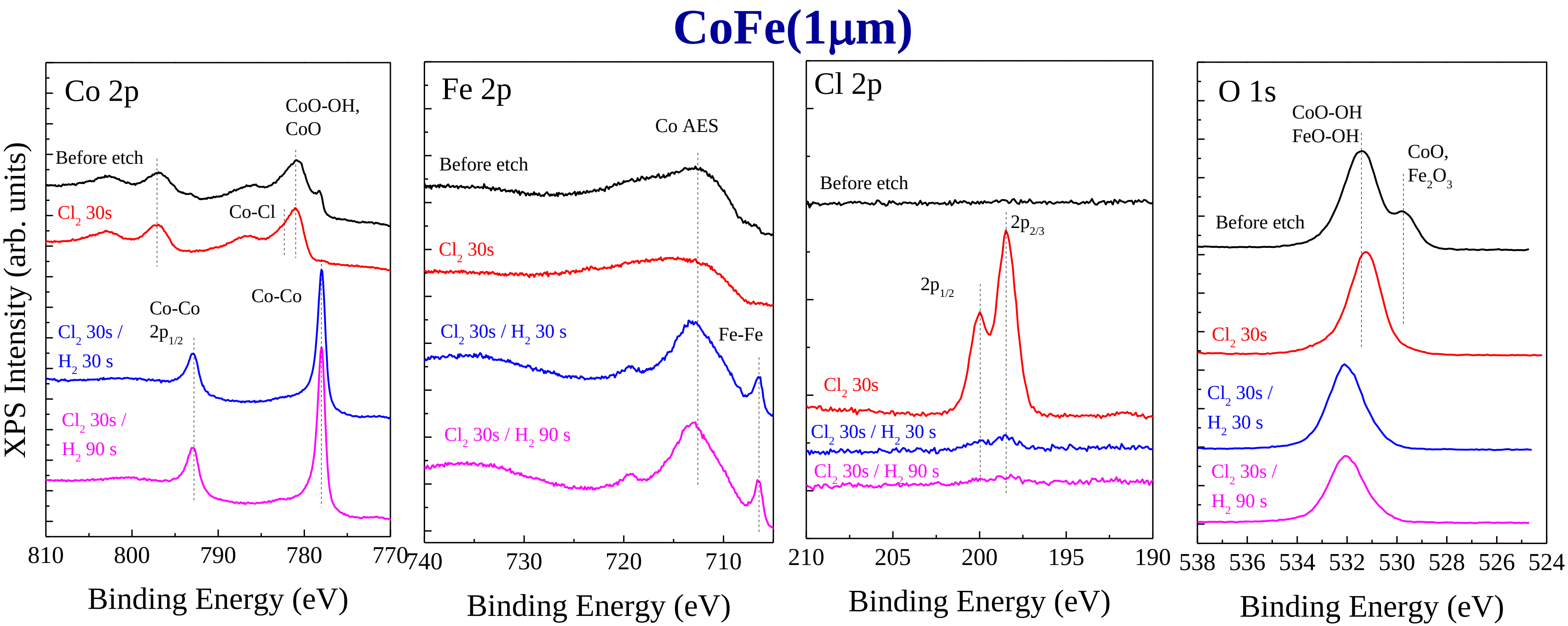
- **H_2 plasma addition enhances the etch rate of Co, which validates the thermodynamic calculation**
- **XPS results show metal chloride layer can be removed by H_2 plasma**

Co/Ni/Fe Etching by Cl_2/H_2



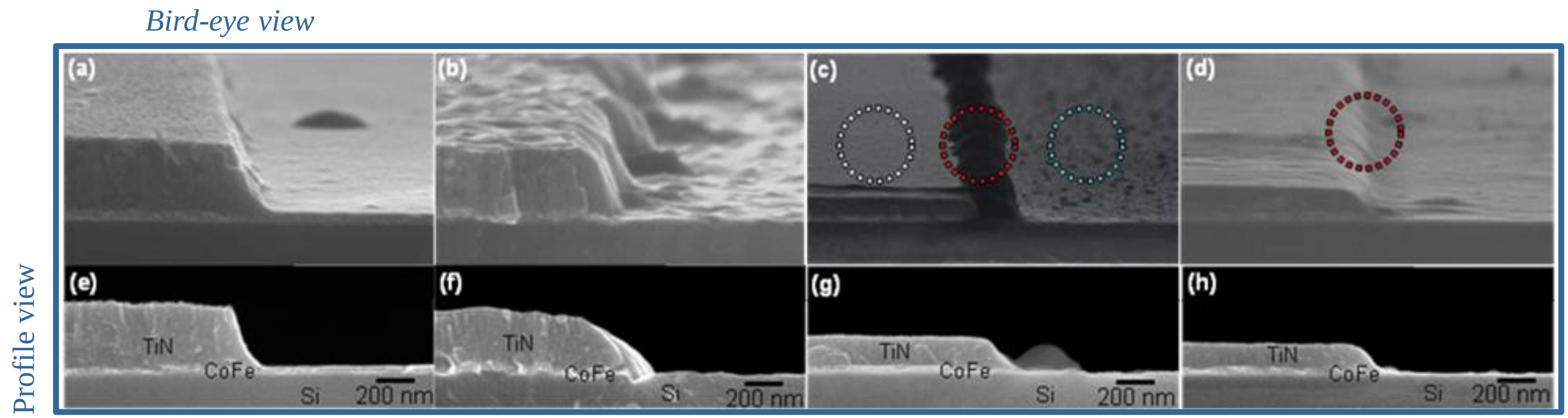
- **H_2 plasma addition enhances the etch rate of Co/Ni/Fe in Cl_2 plasma, which validates the thermodynamic calculation**

CoFe Alloy Etching by Cl_2/H_2



- **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**

CoFe Film Etching by Cl_2/H_2

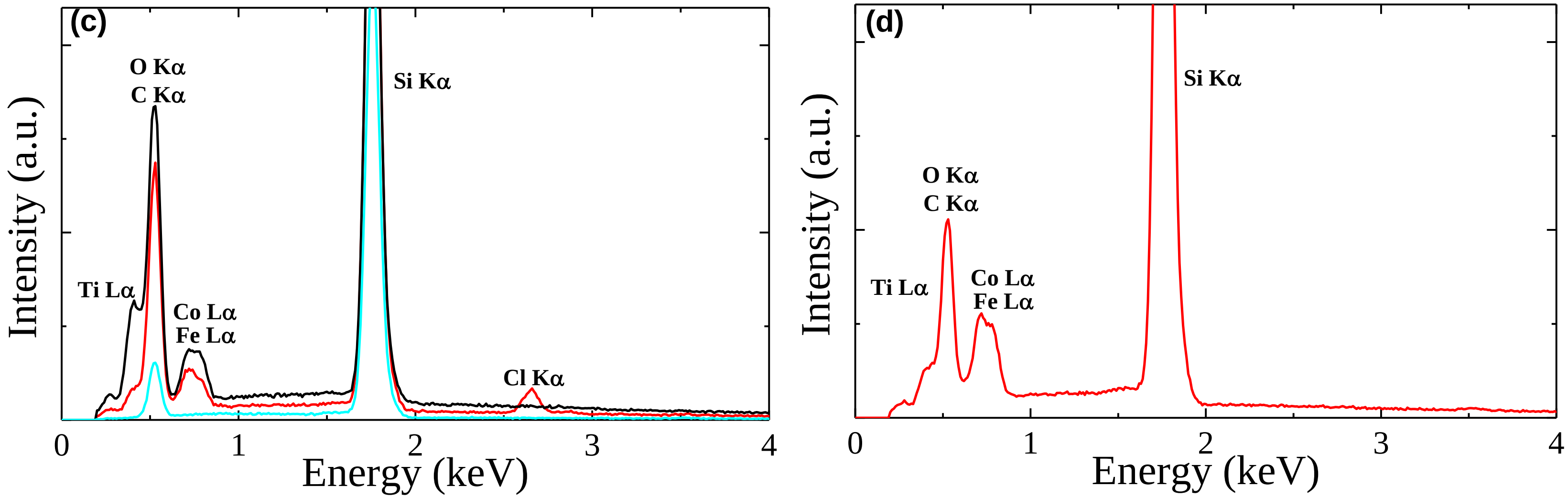


Before etch (CoFe = 45 nm)

Ar plasma exposure (4 min)
20 mTorr pressure

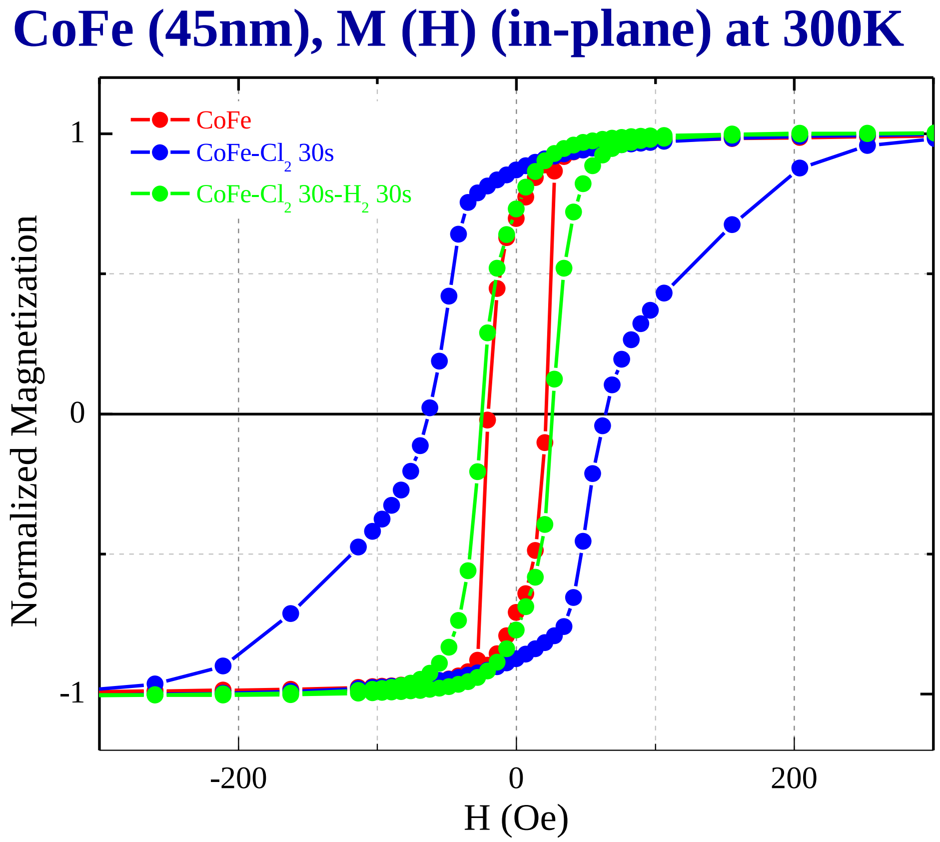
Cl_2 plasma exposure (2 min)
20 mTorr pressure

H_2 plasma exposure (2 min)
20 mTorr pressure



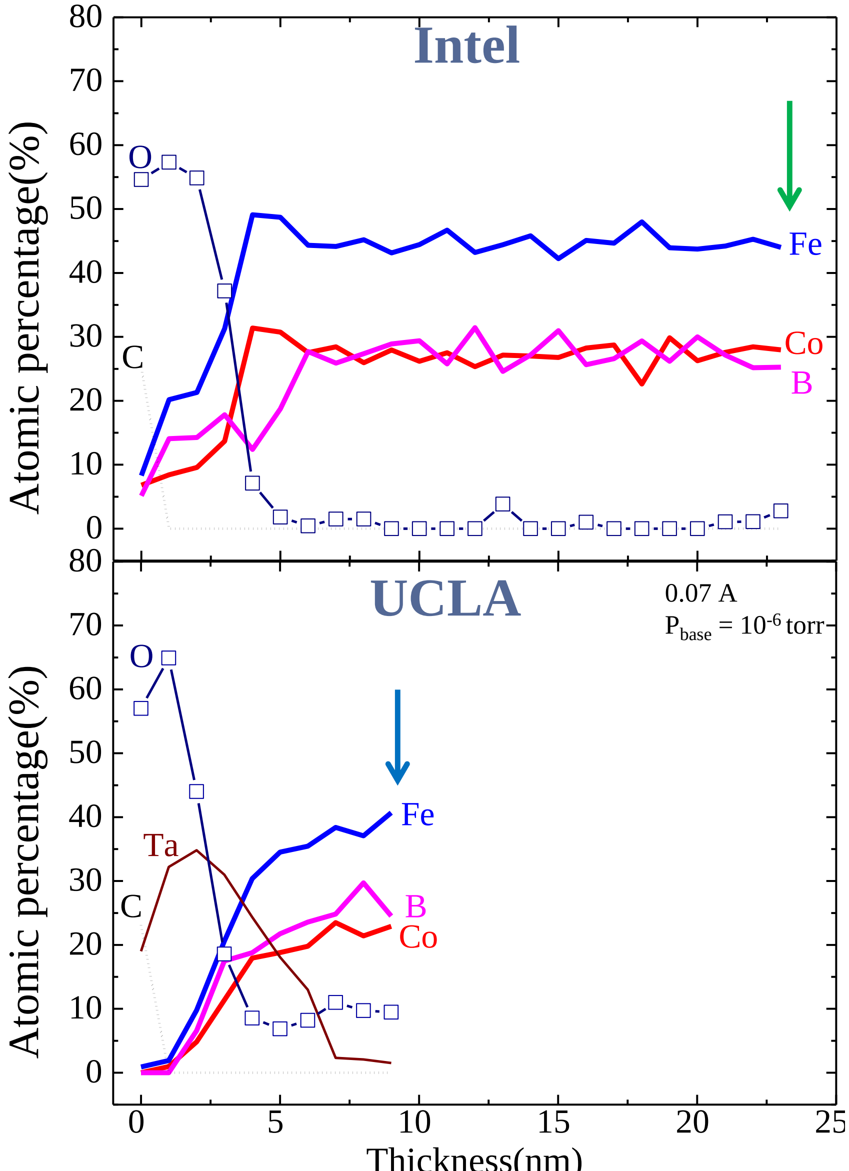
- **EDS confirmed the formation of cobalt and iron chlorides after Cl_2 plasma and their subsequent removal after H_2 plasma**

Magnetic Properties of CoFe (Cl_2-H_2)



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

Intel vs UCLA CoFeB

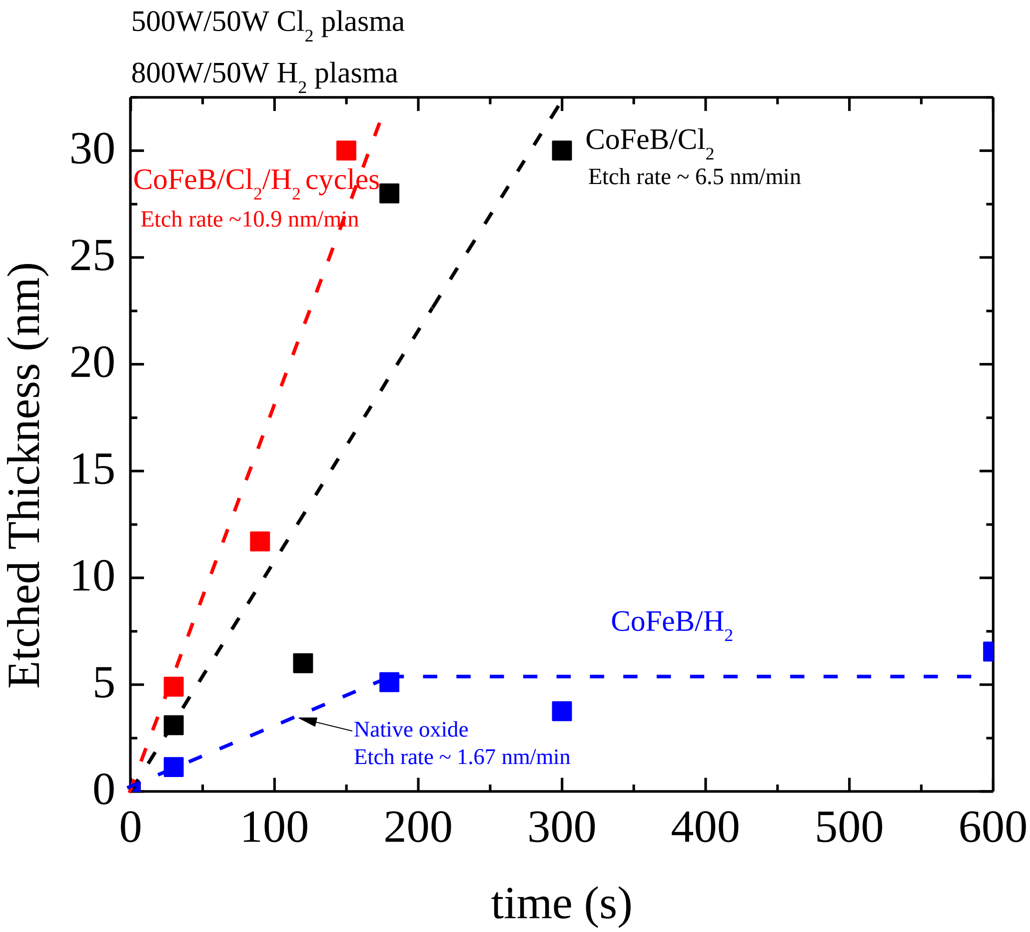


Final: $Co_{29}Fe_{45}B_{26}$
Target: ?
Elemental: $Co_{28}Fe_{44}B_{25}O_3$

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

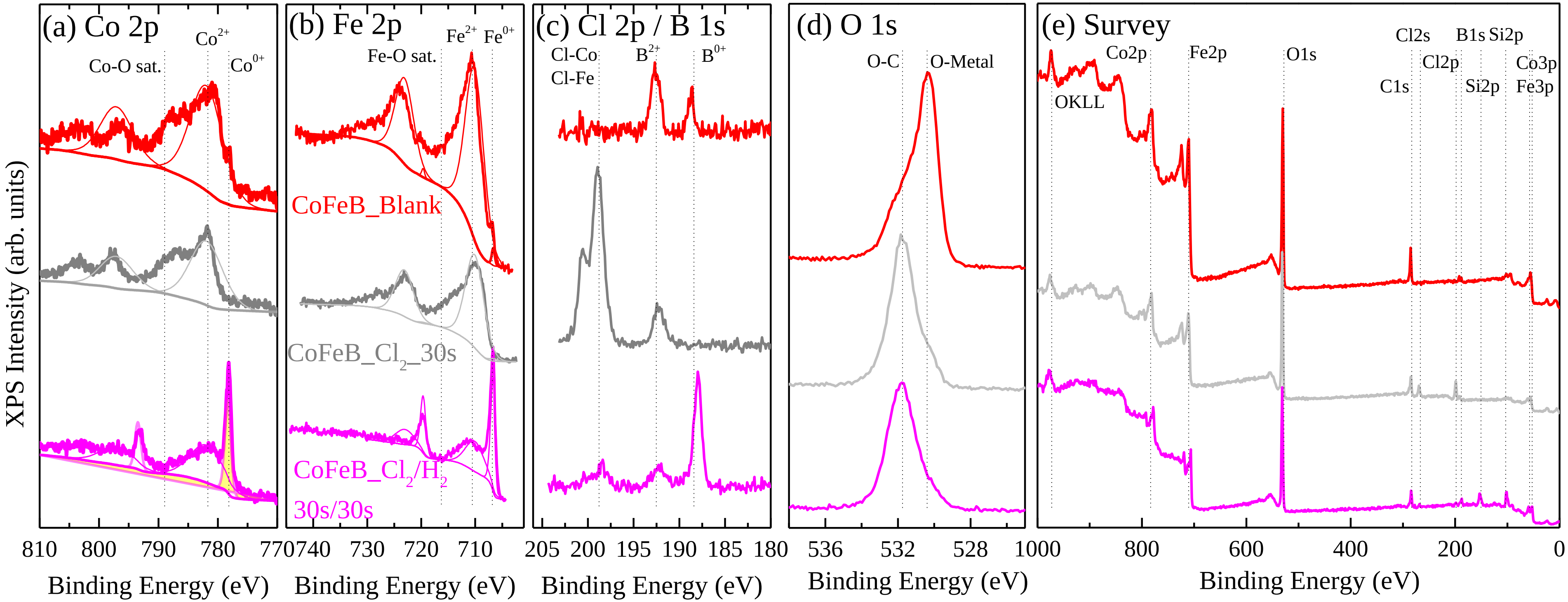
- **Difficulty in using "in-house" deposited CoFeB film for etch studies**
- **Continue to investigate etch chemistries for CoFeB with Intel film**

CoFeB Etching by Cl_2/H_2



- **Etch rate of CoFeB in H_2 plasma saturates after native oxide removal**
- **Sequential exposure results in 40% enhancement over continuous Cl_2 exposure**

XPS of CoFeB Etching by Cl_2/H_2



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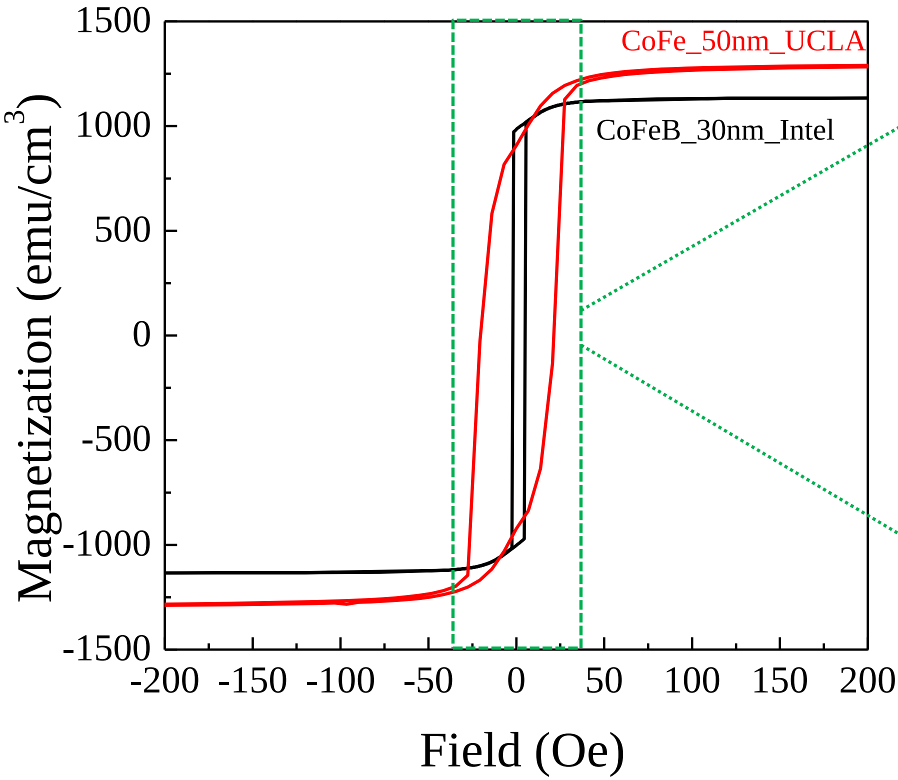
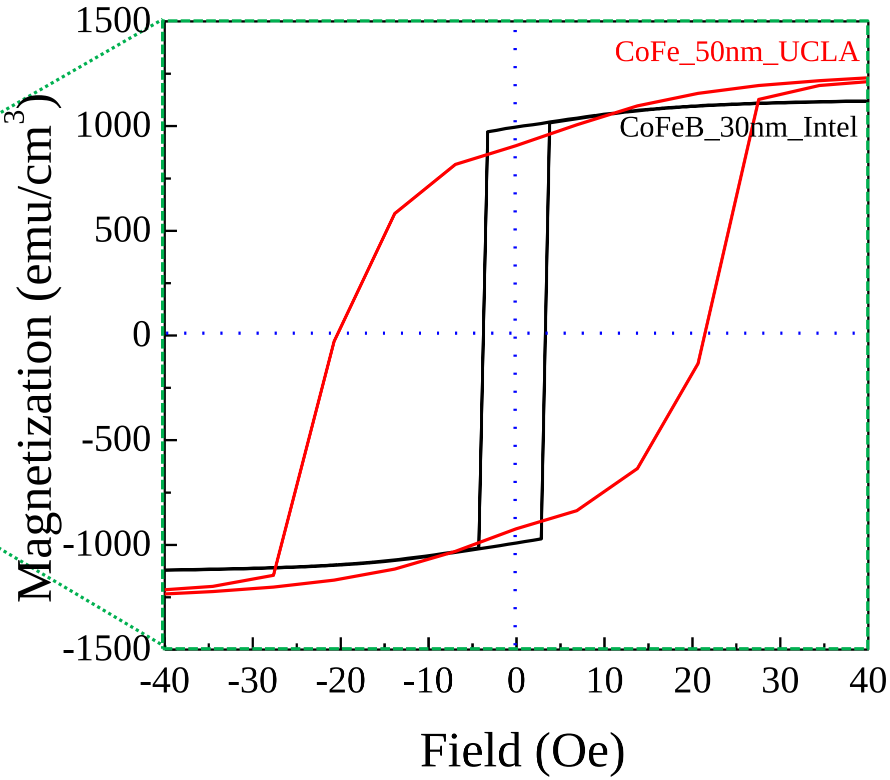
SQUID of CoFe and CoFeB

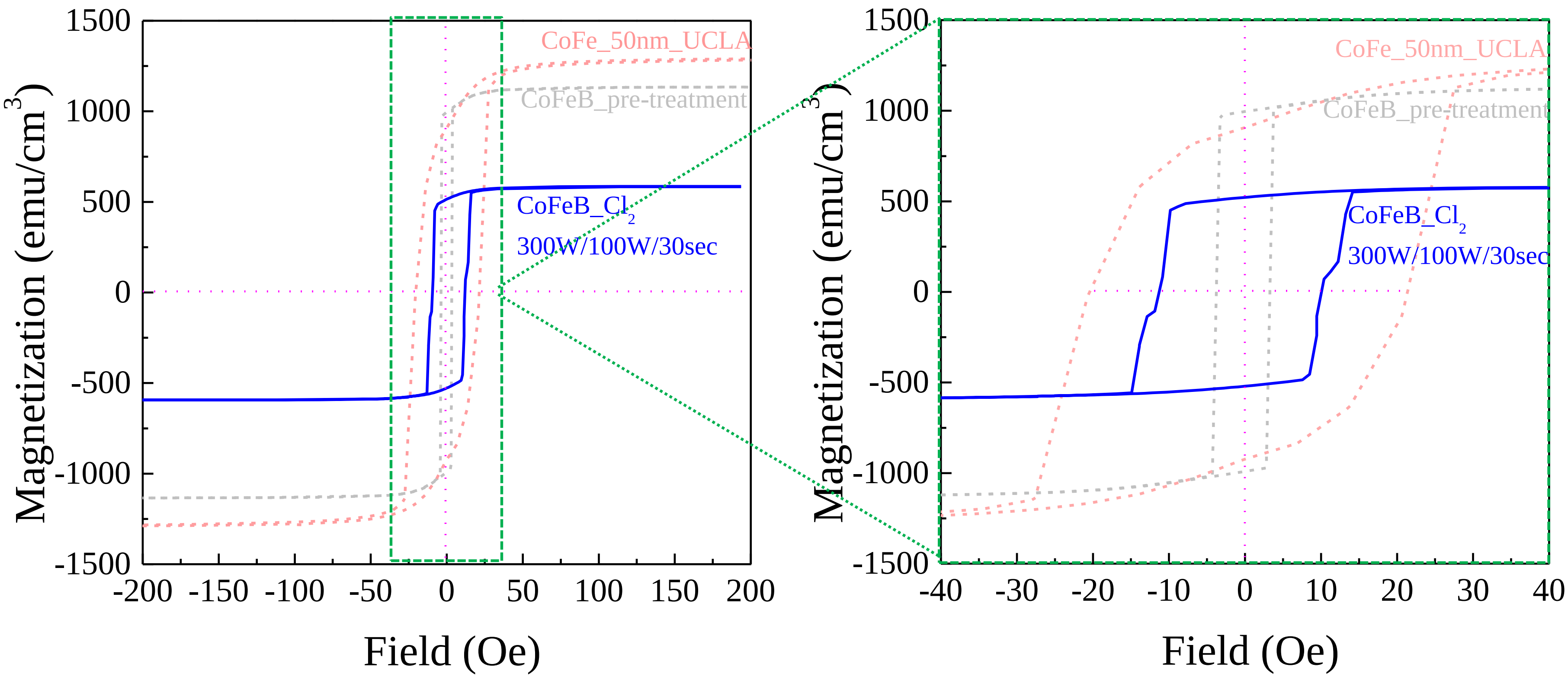




- **Doping with B disrupts the crystallinity of CoFe, causing the coercivity and saturated magnetization to decrease**
- **Coercivity of blank CoFeB (30nm) from Intel is about 3.5Oe which is much smaller than that of CoFe (50nm)**

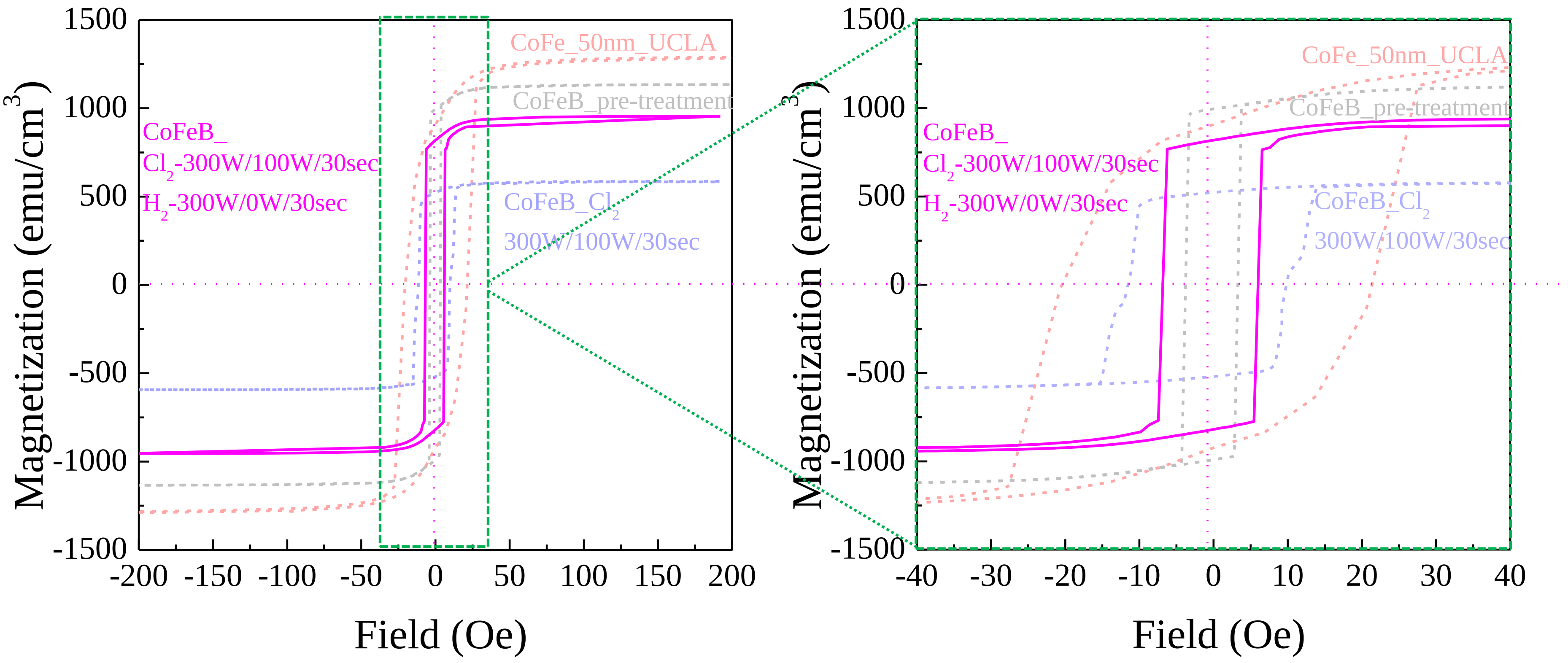
	Coercivity	Ms
CoFe	20.0 Oe	1300
CoFeB	3.5 Oe	1134

SQUID of CoFeB after Cl_2 Etch



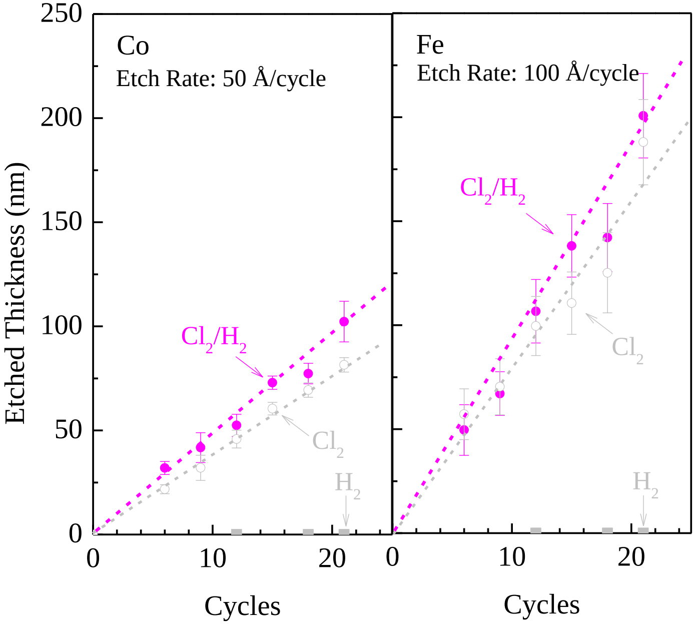
- **30 s exposure to Cl_2 plasma results in formation of metal and boron chloride species, increasing coercivity**

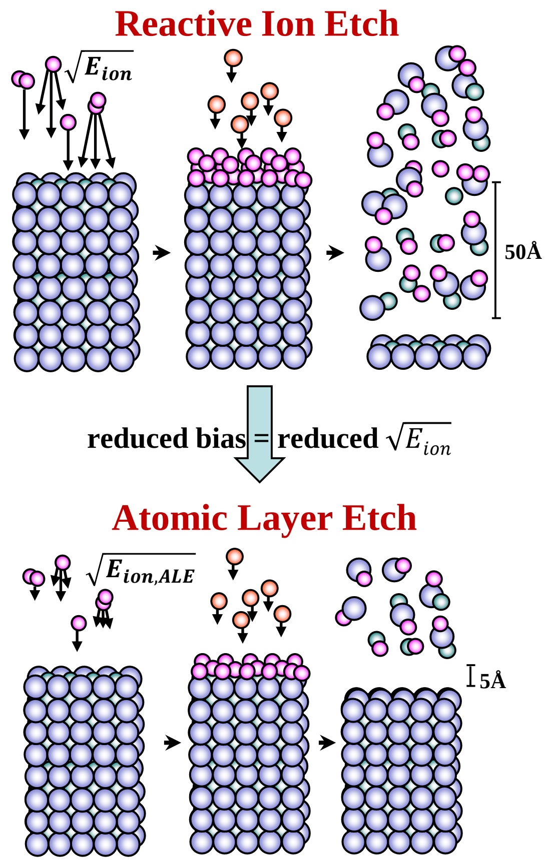
SQUID of CoFeB after Cl_2/H_2 Etch



- **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

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

$$\Downarrow$$

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

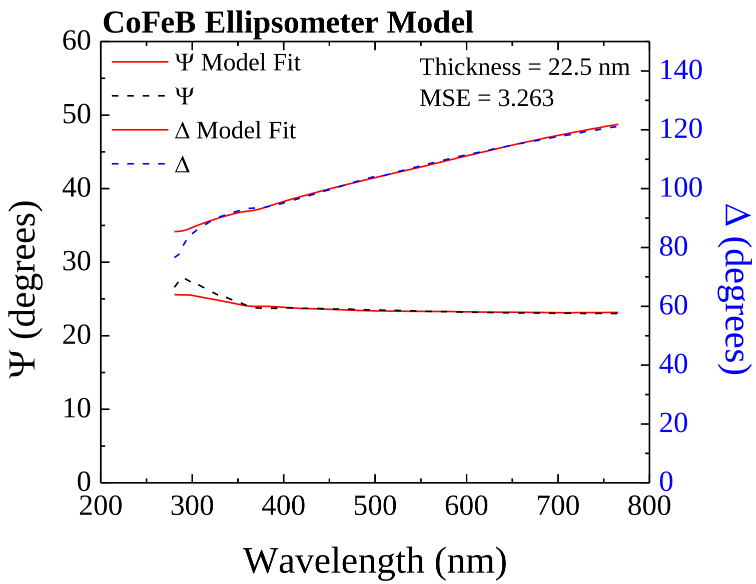
$$\Downarrow$$

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

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

Quantification of ALE

Ellipsometry
(in-situ)

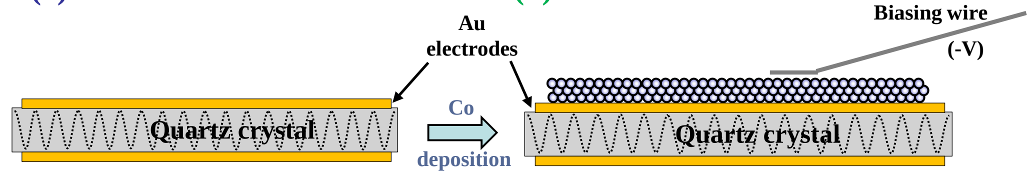


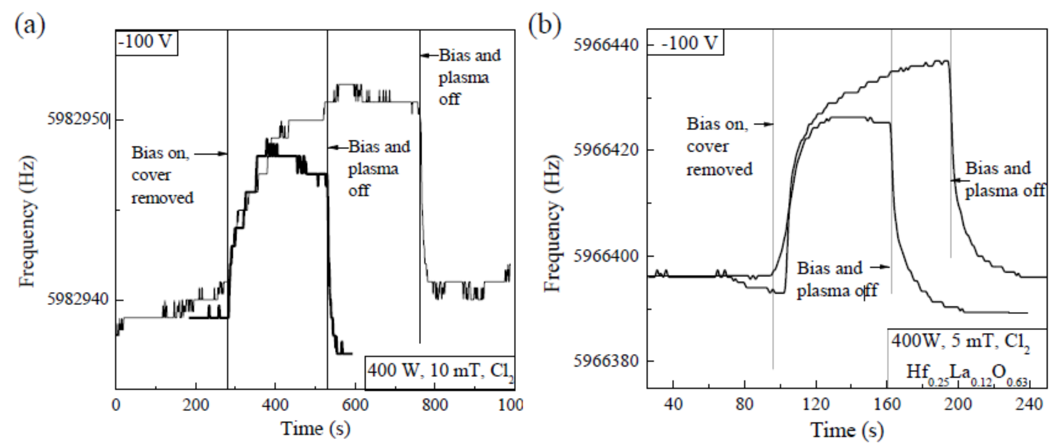
- Ineffective on reflective materials (CoFeB)
- Heavily dependent on degree of surface roughness

QCM
(in-situ)

(a) Unloaded

(b) Loaded



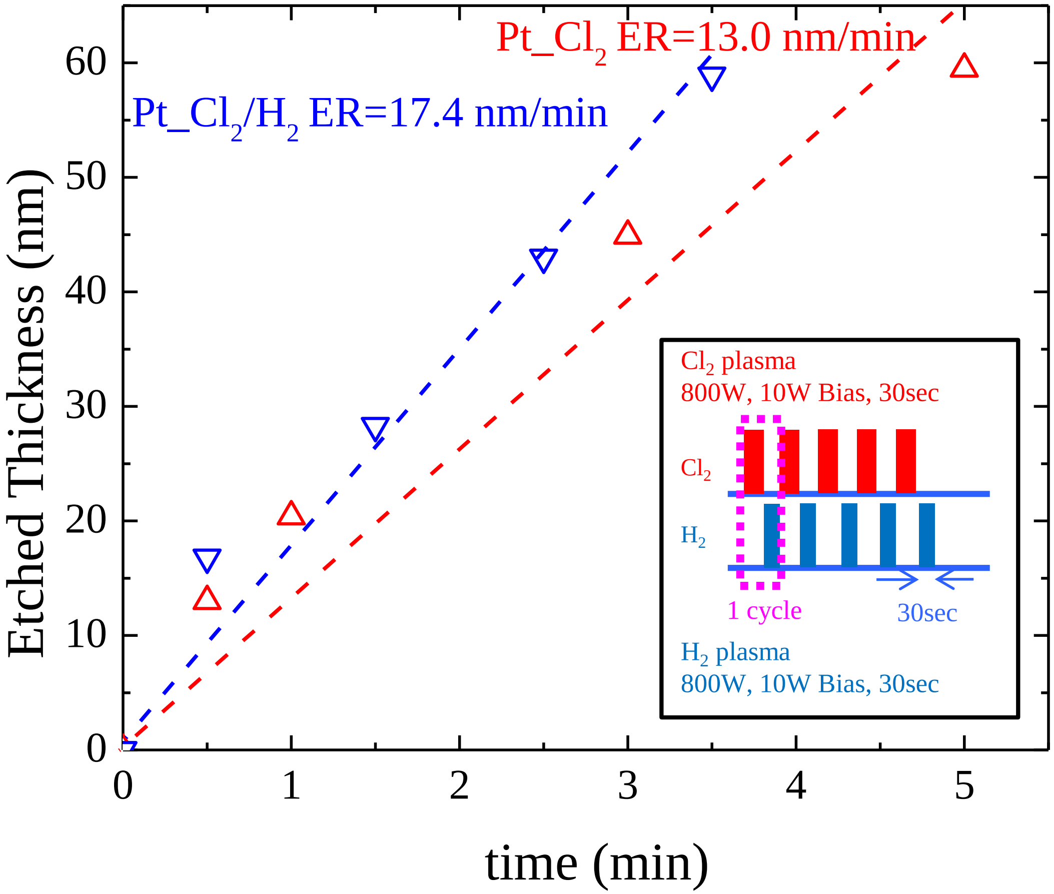


- Difficult to bias substrate due to sample holder
- Use ion beams or ions extracted from a plasma to control the ion energy

- **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**

Pt Etching by Cl_2/H_2

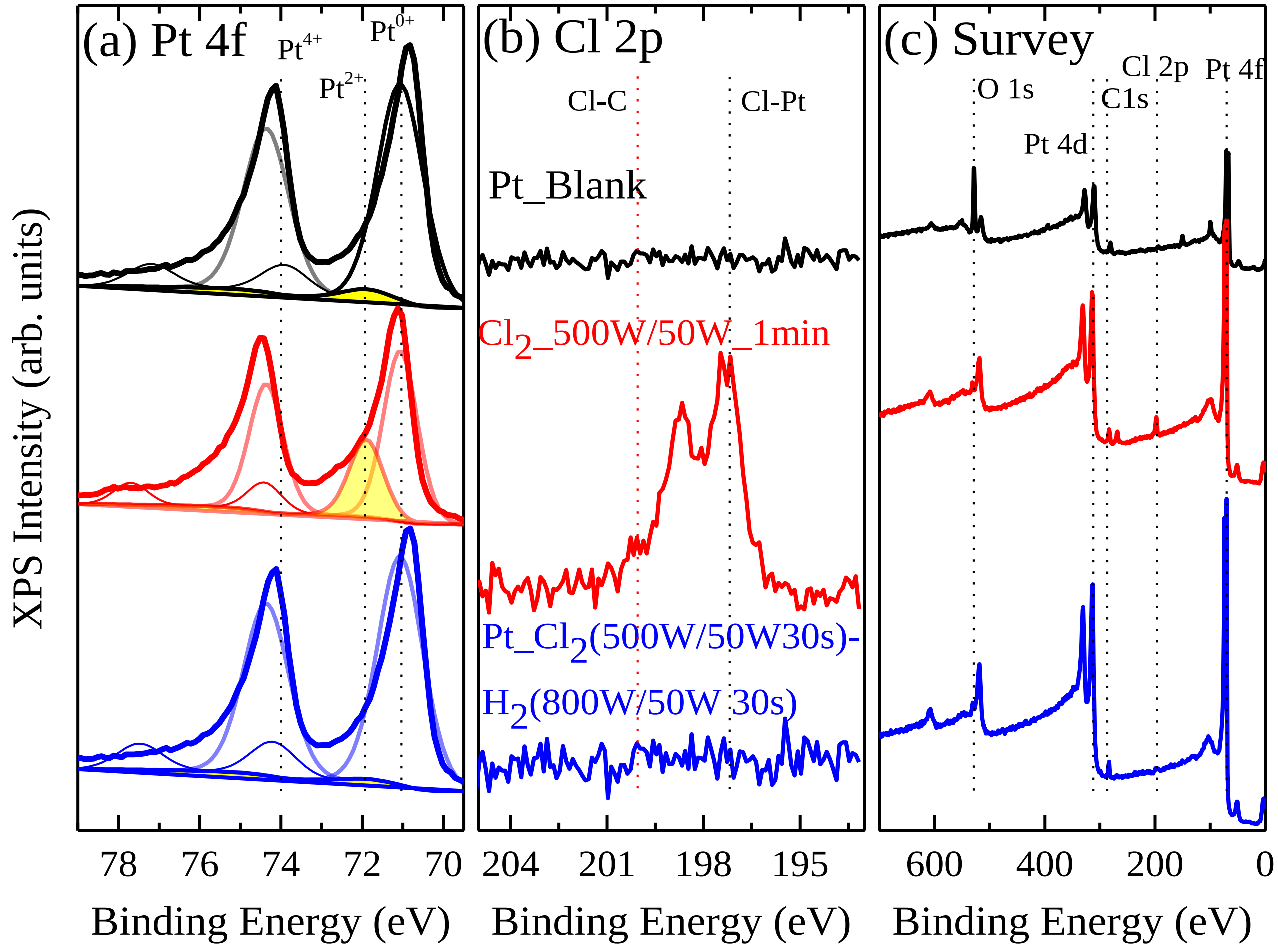
Etch rate measured by SEM



- **The etch rate is enhanced by 33% through the use of sequential Cl_2-H_2 exposure, but could increase by reducing bias and suppressing sputtering component**

Pt Etching by Cl_2/H_2

XPS Composition



- **Similar to the result from CoFe and CoFeB, exposure to H_2 plasma removes metal chloride, resulting in increased etch rate**

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")

- **SRC ERC EHS TeleSeminar, March 5, 2015**

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**