Selective and Directional Patterning of Ni for EUV Application

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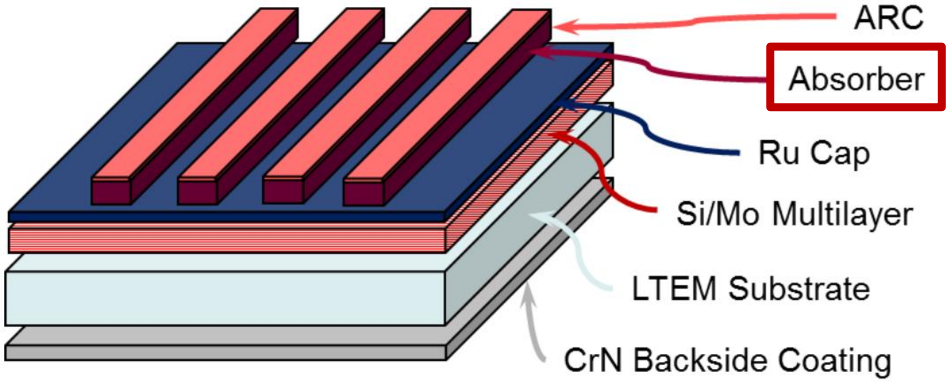
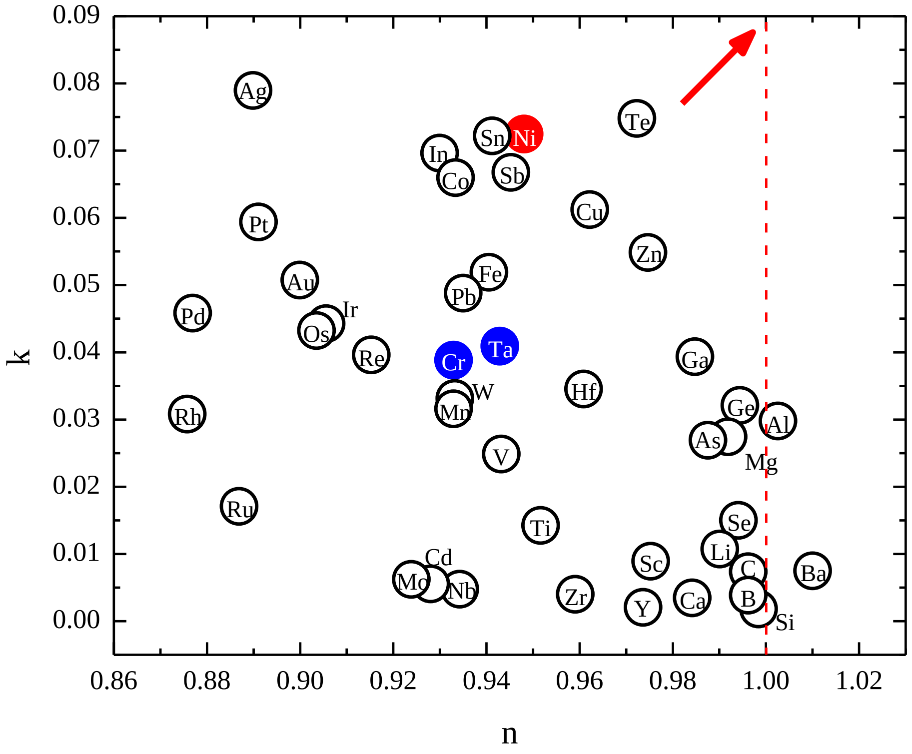
EUV Absorbing Material Selection

- Properties of absorber material are of crucial importance
  - Atomic level flatness
  - Vertical sidewall profile
  - ARC layer compatibility
  - Ru capping layer compatibility
  - High absorbing capability
- Complex refractive index
  - $\bar{n} = n + ik$
- Refraction occurs when light travels through media
  - n close to 1 preferred
- Electric field intensity decreases exponentially with k:
  - $E(x,t) = e^{-2\pi kx/\lambda_0} Re[E_0 e^{i(kx-\omega t)}]$
  - high k preferred





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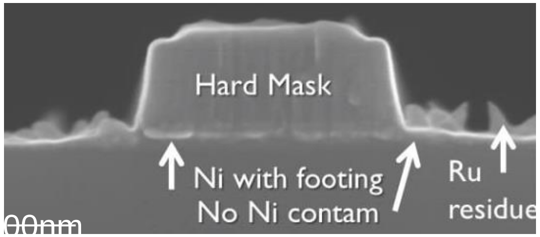
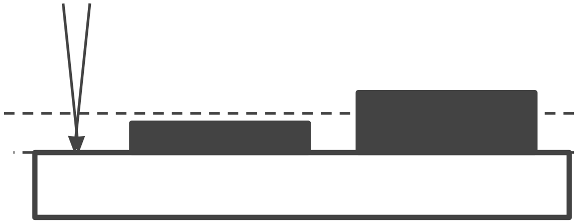
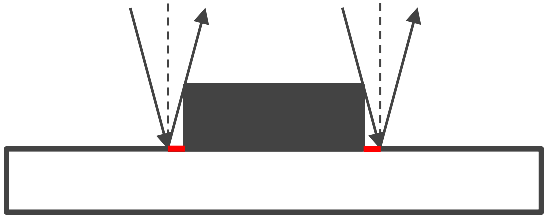
The Need for Thinner Absorber





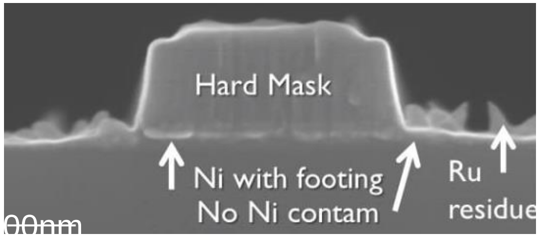


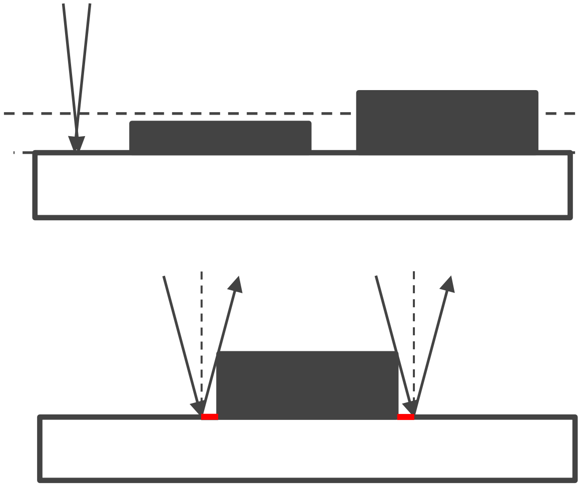
	Cr	**Ta**	**TaN**	**TaBN**	**Ni**
n	0.933	0.944	0.927	0.953	0.948
k	0.0383	0.0403	0.0431	0.031	0.073
Thickness	70 nm	60 nm	60 nm	50~80 nm	30 nm
Etching	Ion milling	Cl_2 based	Cl_2 based	Cl_2 based	--
Selectivity, to Ru	> 5:1	—	100:1	—	'high'
Etch bias	40~60 nm	—	—	10 nm	—

- Thick absorbers result in loss of fidelity (depth of focus, shadowing effect)
- Absorbers are primarily patterned by sputtering (high anisotropy, low selectivity, mask damage and sidewall re-deposition)
- Need a chemical etching process for high anisotropy, selectivity and profile control

V. Philipsen *et al.*, (2017), *Proc. SPIE* Vol. 10143

Need to Pattern Thinner Absorber





Matsui, N., et al. (2002). "Etching characteristics of magnetic materials (Co, Fe, Ni) using CO/NH3 gas plasma for hardening mask etching." Vacuum **66**(3-4): 479-485.
Cho, H. N., et al. (2007). "High density plasma etching of nickel thin films using a Cl2/Ar plasma." Journal of Industrial and Engineering Chemistry **13**(6): 939-943.
Williams, K. R., et al. (2003). "Etch rates for micromachining processing-Part II." Journal of Microelectromechanical Systems **12**(6): 761-778.

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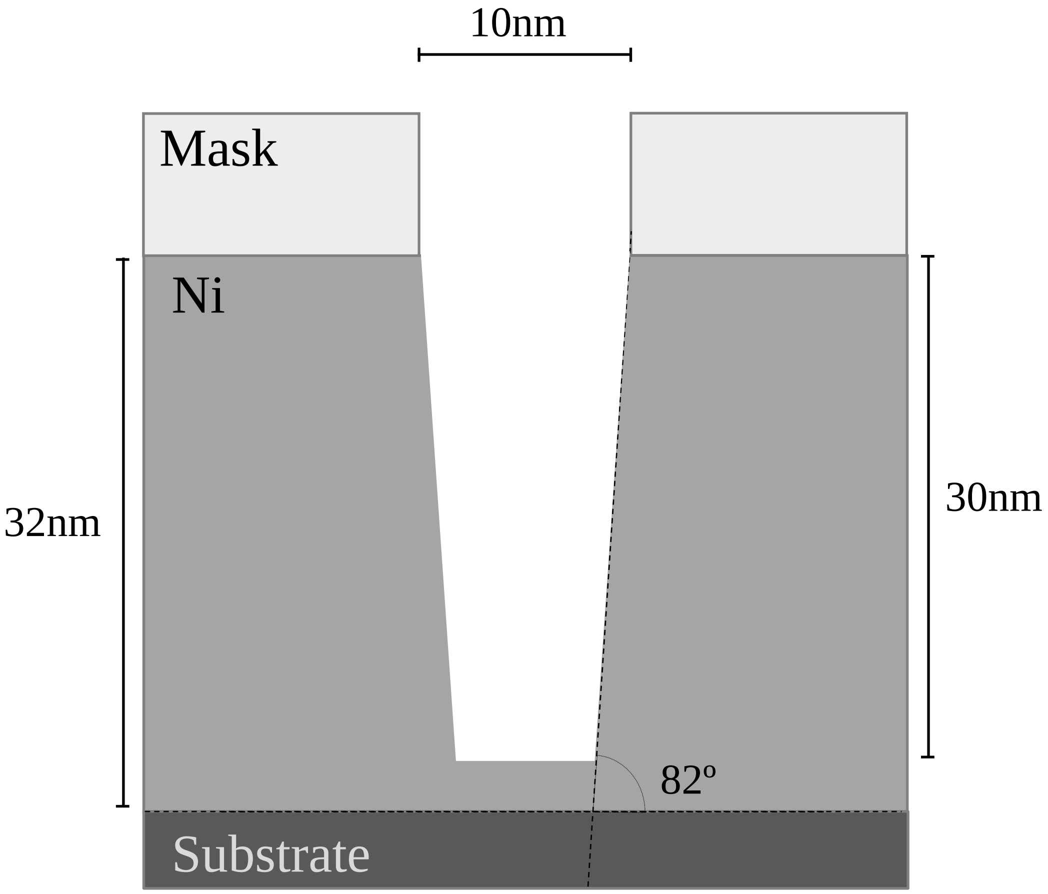
Etchant Phase	**Etchant**	**ER (nm/min)**
Solution	126 HNO_3 : 60 H_2O : 5 NH_4F	13
	80% H_3PO_4 + 5% HNO_3 + 5% HAc + 10% H_2O	29
	30% $FeCl_3$ + 4% HCl + H_2O	21
	3 HCl : 1 HNO_3 : 2 H_2O	100
	50 H_2SO_4 : 1 H_2O_2	380
Gas	Ar^+ 500 V ion milling	66
	50% Co + 50% NH_3 plasma	30 ~ 90
	20% Cl_2 + 80% Ar plasma	40

Hybrid Ni RIE/ALE Process



1): Alternating reactive ion etch
Goal: Etch bulk of Ni layer, $\Theta_{SW}=82°$

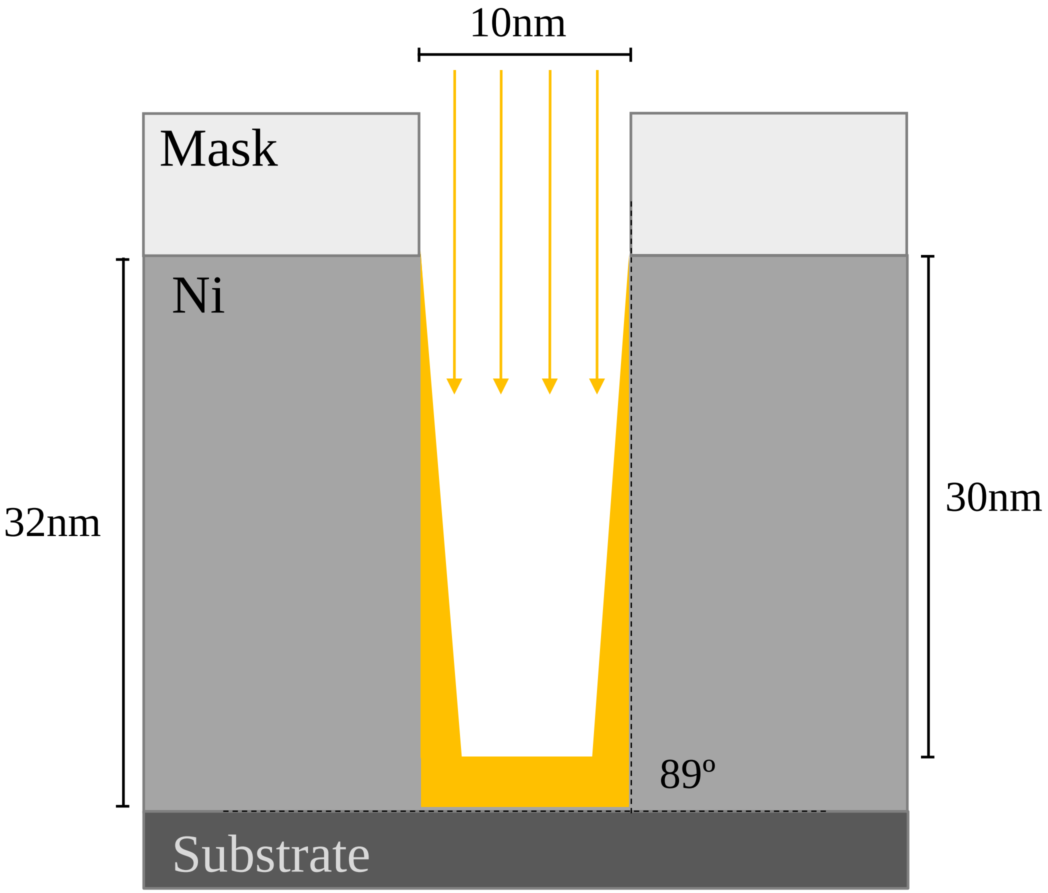
Cl_2	$500W_s$	30s
H_2	$-100V_b$	30s

2) Directional surface modification
Goal: Directionally generate oxide (LoS)

O_2	$500W_s$ $-100V_b$	300s

- Bulk etch of Ni feature using alternating Cl_2/H_2 RIE chemistry, resulting in non-ideal sidewall angle (~82°) and hydrogen terminated surface

Hybrid Ni RIE/ALE Process



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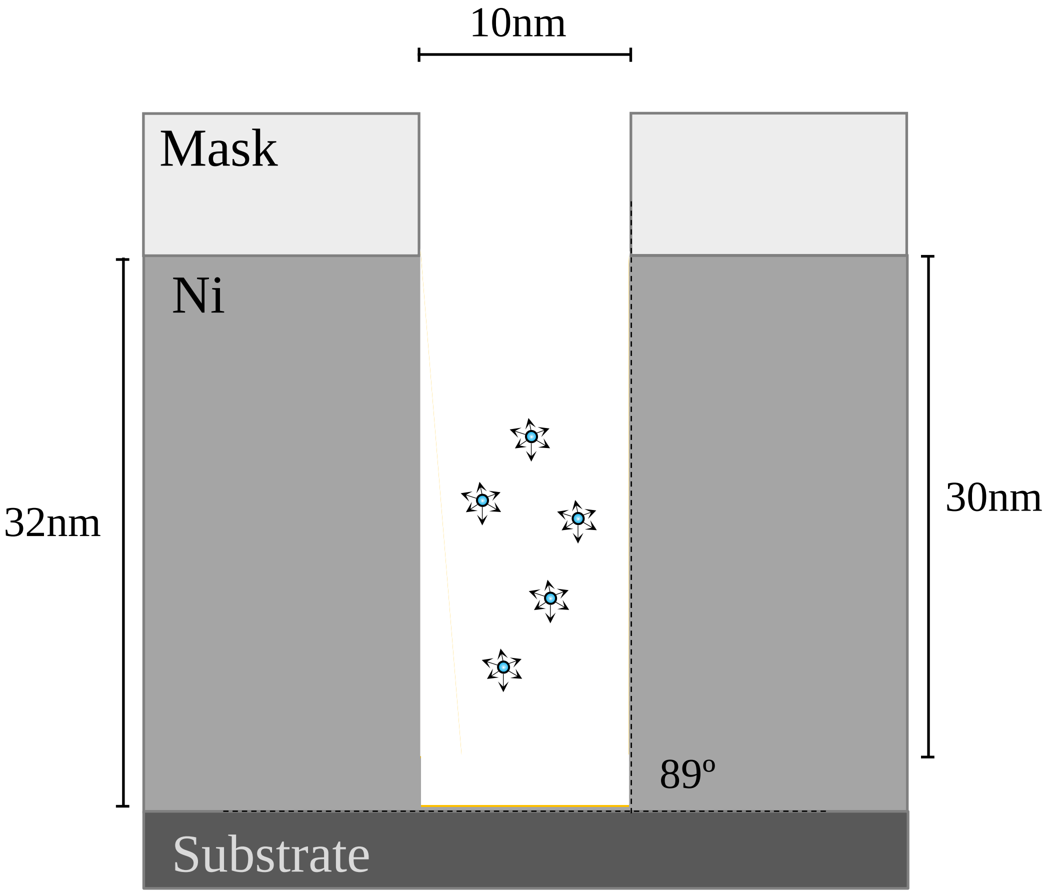
- Directional surface modification will be used to modify sidewall contrast to specified range (90°±3°)

Hybrid Ni RIE/ALE Process



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Goal: Directionally generate oxide (LoS)

O_2	$500W_s$ $-100V_b$	300s

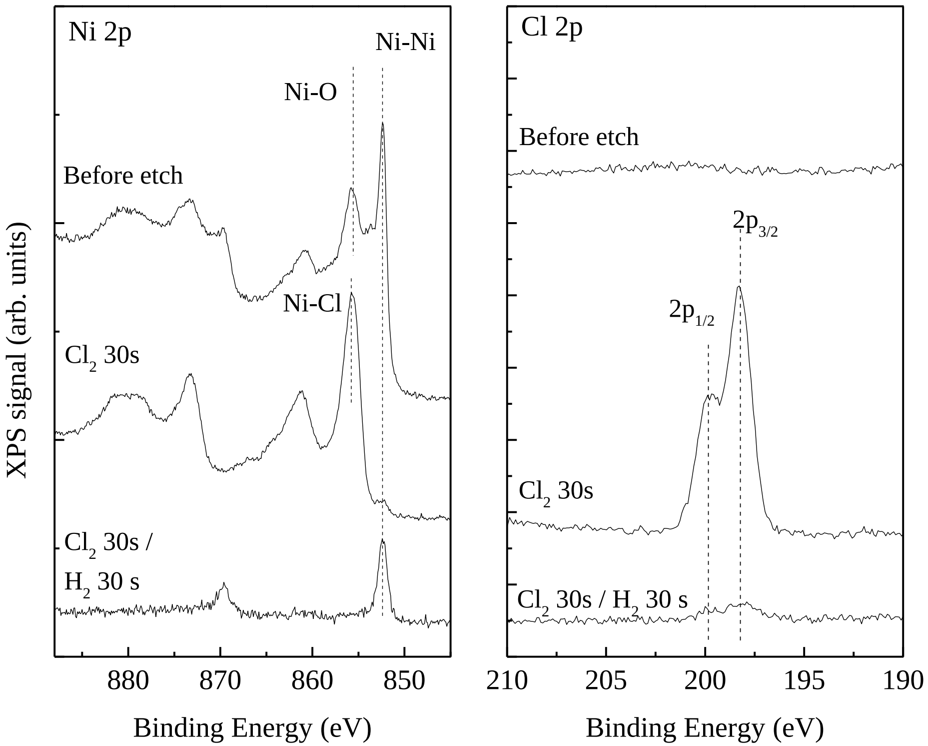
3) Organic vapor etch

Goal: Remove oxide, trim Θ_{SW}=90°

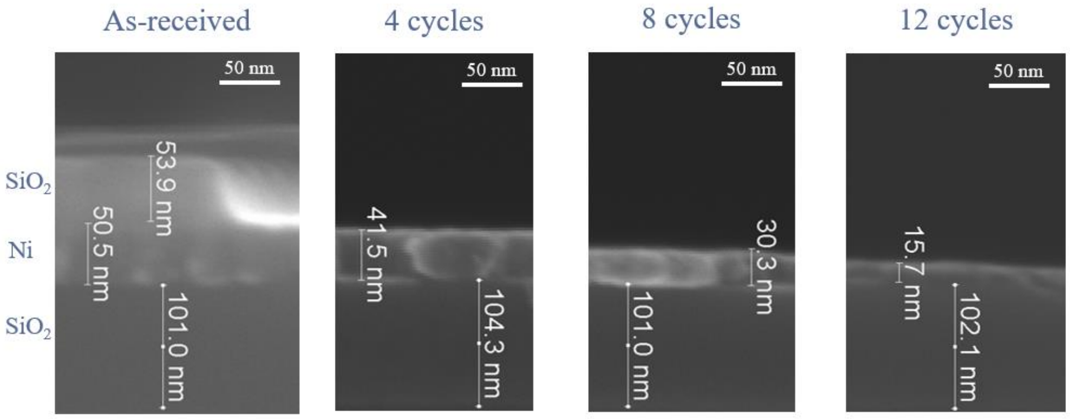
Formic acid (g)	80°C 150 Torr	50s

- Organic vapor etch will be used to achieve the self-limiting atomic layer etching, thereby trimming sidewall to specified range (90°±3°)

Reactive Ion Etching of Ni in Cl_2/H_2



Chemistry	Flow Rate (sccm)	Power (W)	Bias (V)	Pressure (mTorr)	Time (sec)
Cl_2	60	500	-50	15	30
Ar	10				
H_2	15	800	-100	20	30



- Surface composition measured by XPS
  - 30 seconds of chlorine plasma exposure fully chlorinated Ni surface
  - Subsequent 30 seconds of hydrogen plasma exposure removed previously chlorinated layer, exposing Ni underneath
- Thickness reduction observed from SEM confirms etching validity

Thermodynamics Assessment

	Ni		**NiO**	
	Reaction	ΔG_{rxn} (kJ/mol)	Reaction	ΔG_{rxn} (kJ/mol)
Acetic acid	$Ni(s)+2CH_3COOH(l) \rightarrow Ni(CH_3COO)2(aq)+H_2(g)$	-4.3	$NiO(s)+2CH_3COOH(l) \rightarrow Ni(CH_3COO)2(aq)+H_2O(g)$	-29.8
	$Ni(s)+2CH_3COOH(g) \rightarrow Ni(CH_3COO)2(aq)+H_2(g)$	NA	$NiO(s)+2CH_3COOH(g) \rightarrow Ni(CH_3COO)2(aq)+H_2O(g)$	NA
Formic acid	$Ni(s)+2HCOOH(l) \rightarrow Ni(HCOO)2(aq)+H_2(g)$	-41.4	$NiO(s)+2HCOOH(l) \rightarrow Ni(HCOO)2(aq)+H_2O(g)$	-66.9
	$Ni(s)+2HCOOH(g) \rightarrow Ni(HCOO)2(aq)+H_2(g)$	-62.7	$NiO(s)+2HCOOH(g) \rightarrow Ni(HCOO)2(aq)+H_2O(g)$	-79.7
Acetylacetone	$Ni(s)+2acac(l) \rightarrow Ni(acac)_2(aq)+H_2(g)$	NA	$NiO(s)+2acac(l) \rightarrow Ni(acac)_2(aq)+H_2O(g)$	NA
	$Ni(s)+2acac(l) \rightarrow Ni(acac)_2(aq)+H_2(g)$		$NiO(s)+2acac(g) \rightarrow Ni(acac)_2(aq)+H_2O(g)$	
Hexafluoro-acetylacetone	$Ni(s)+2hfac(l) \rightarrow Ni(hfac)_2(aq)+H_2(g)$	NA	$NiO(s)+2hfac(l) \rightarrow Ni(hfac)_2(aq)+H_2O(g)$	NA
	$Ni(s)+2hfac(g) \rightarrow Ni(acac)_2(aq)+H_2(g)$		$NiO(s)+2hfac(g) \rightarrow Ni(hfac)_2(aq)+H_2O(g)$	

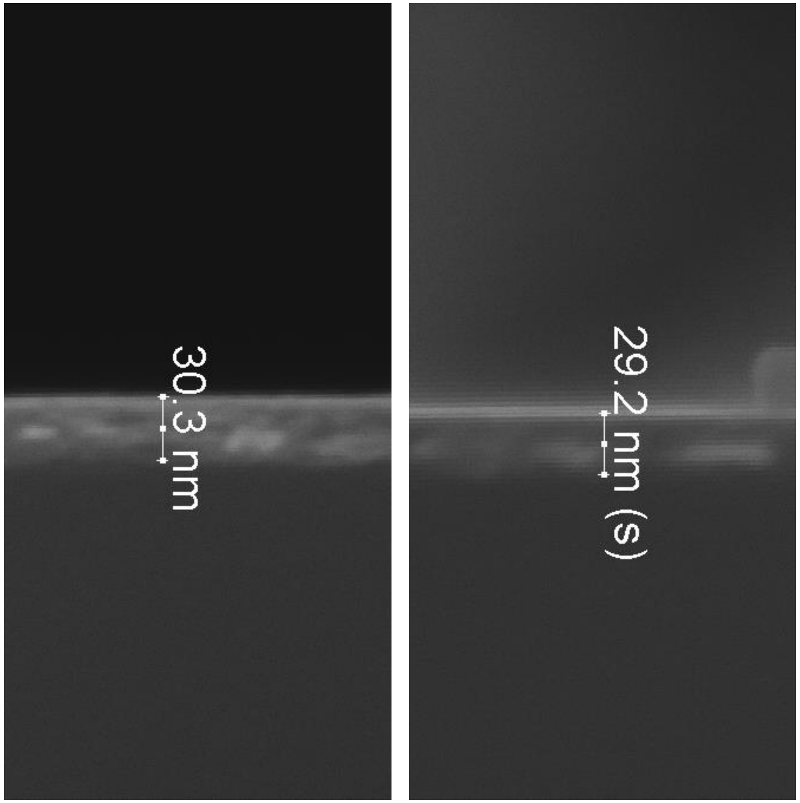
- Formic acid is able to etch Ni and NiO according to thermodynamic data
- Gibbs free energy of reaction suggests oxidation enables the etching of Ni

Calculation done at 25°C, 1 atm, data obtained from HSC

Gas Phase Etching of Ni

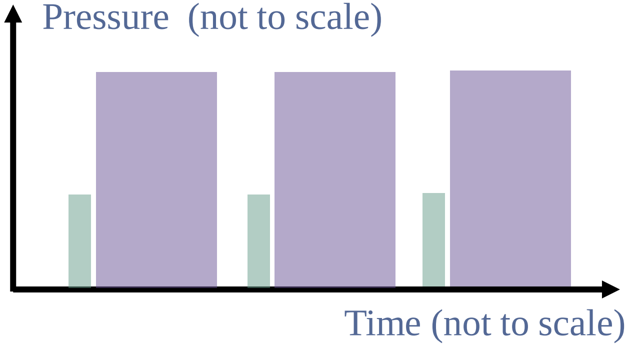
Chemistry	FA vapor
Temperature (°C)	80
Pressure (Torr)	350
Time (min)	180

- 3 hours of continuous exposure
- Exposure temperature same as that in solution phase
- Relatively high pressure (half of atmospheric pressure) to maintain the concentration
- SEM shows negligible thickness change

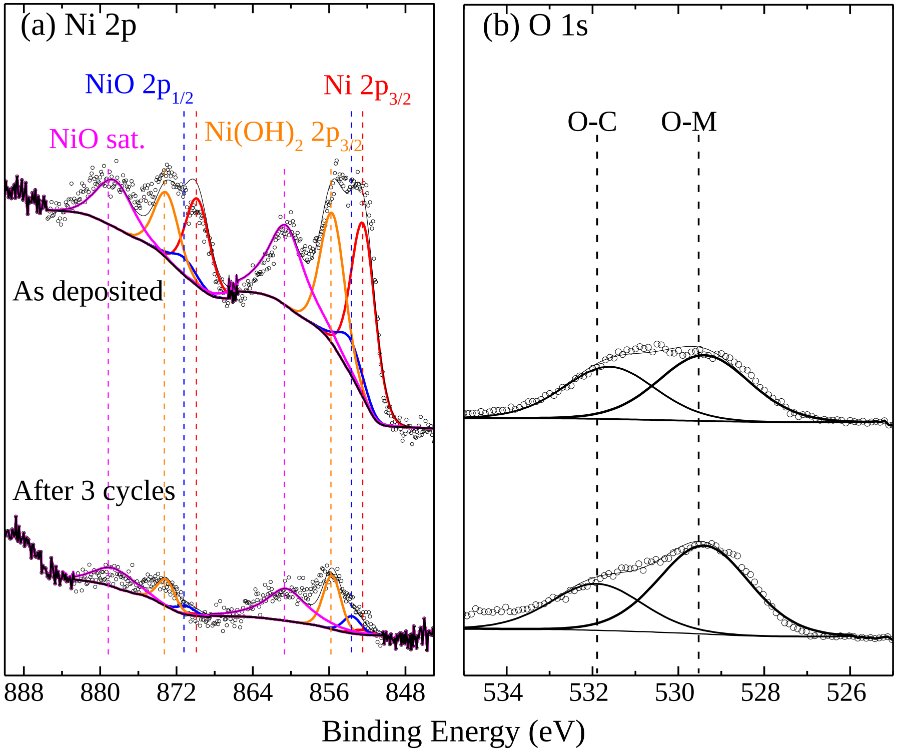

As-received After 3 hours

Gas Phase Etching of Ni via Oxidation

O_2/FA
Cyclic Etch



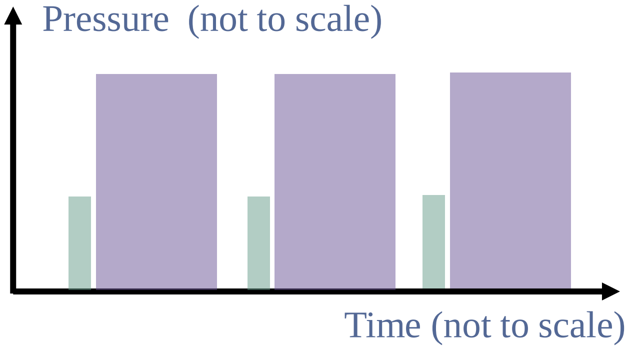
Chemistry	Temperature (℃)	Power (W)	Bias (V)	Pressure (Torr)	Time (min)
O_2	25	500	-50	0.009	2
FA	80	NA	NA	350	60

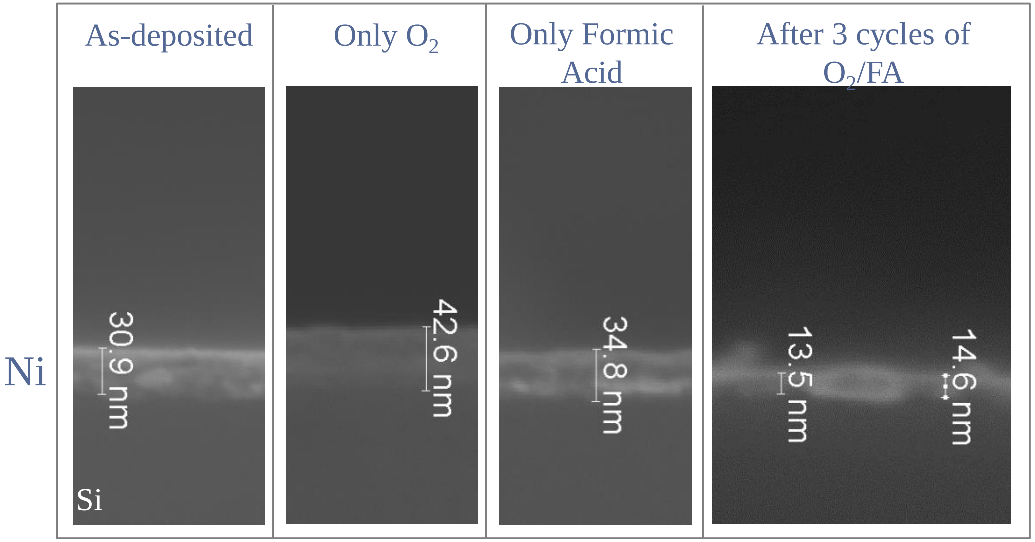


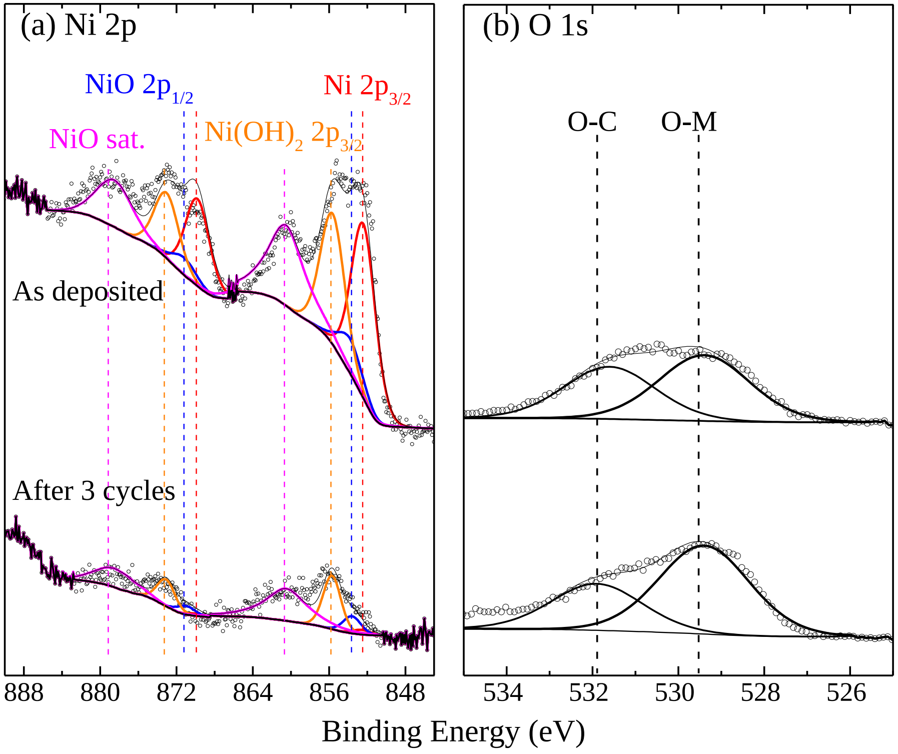
- Reduction of Ni signal confirmed removal of Ni
- Metal oxide peak at 529.5eV confirmed formation of NiO

Gas Phase Etching of Ni via Oxidation

O_2/FA
Cyclic Etch



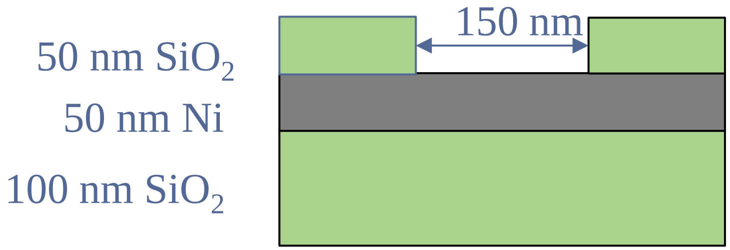




- Cross-sectional SEM structurally confirm decrease of Ni thickness
- Surface roughens and ~16 nm removed after 3 cycles, etch rate ~5.3 nm/cycle

Gas Phase Etching of Patterned Ni

Chemistry	Temperature (℃)	Power (W)	Bias (V)	Pressure (Torr)	Time (min)
O_2	25	500	-50	0.009	2
FA	80	NA	NA	350	60

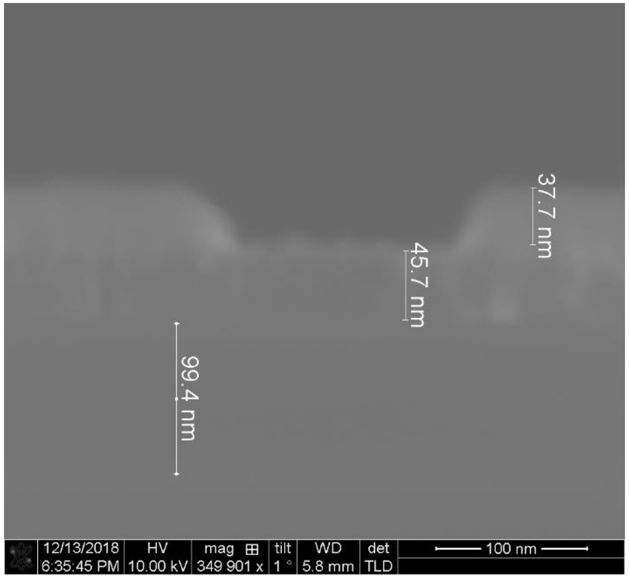


50 nm SiO_2

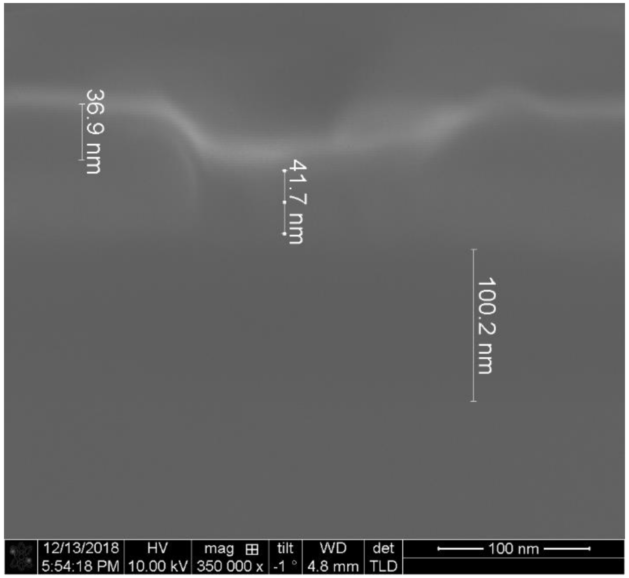
50 nm Ni

100 nm SiO_2

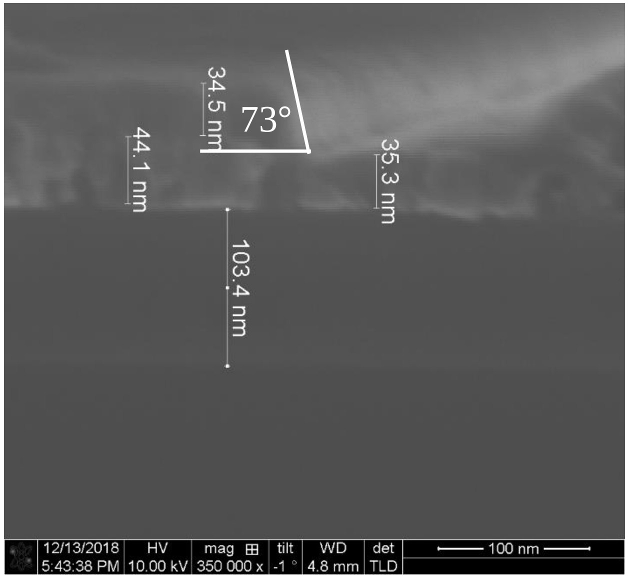
As-received



2 cycles



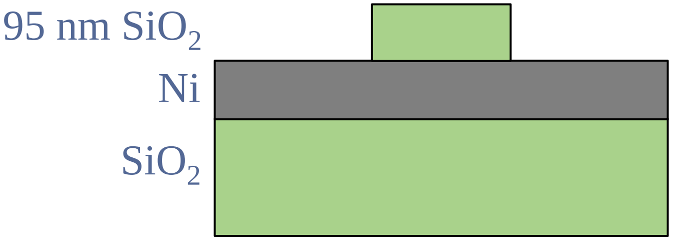
4 cycles

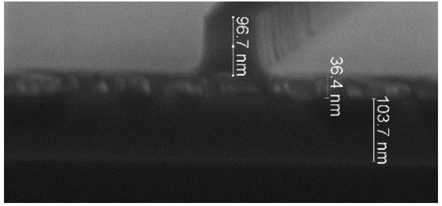
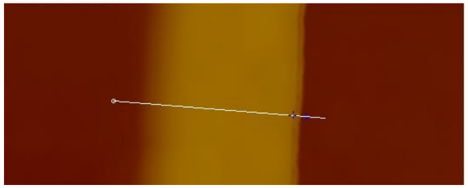
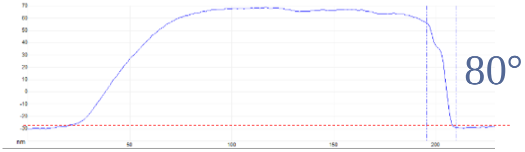
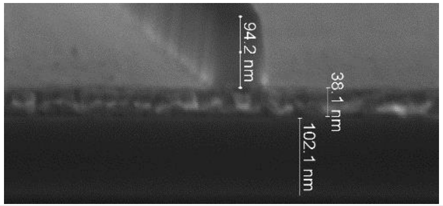
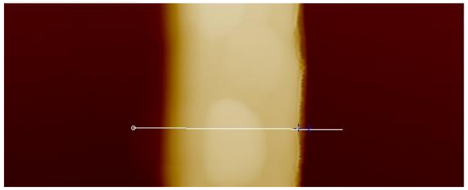
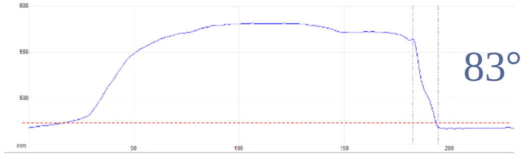
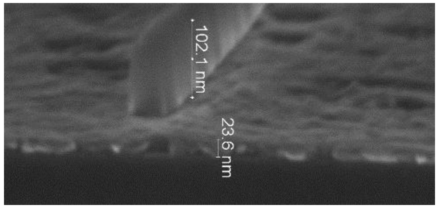
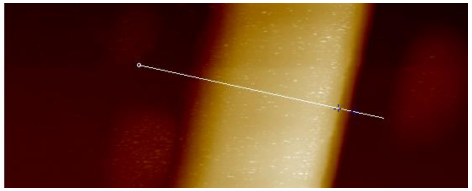
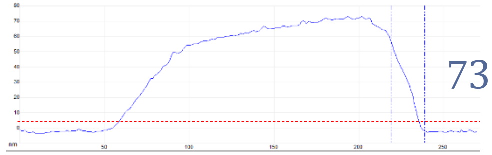


- Same process applied to patterned samples provided by Intel
- ~ 10 nm of Ni removed after 4 cycles, etch rate ~ 2.5 nm/cycle

Gas Phase Etching of Isolated Ni Line

Chemistry	Temperature (℃)	Power (W)	Bias (V)	Pressure (Torr)	Time (min)
O_2	25	500	**0**	0.009	2
FA	80	NA	NA	350	60



	SEM	**AFM**	**AFM**
As-rec'd			 80°
2 cycles			 83°
6 cycles			 73°

- Asymmetric profile comes from sidewall-measuring AFM tips
- Sidewall tapered after 6 cycles

Gas Phase Etching of Isolated Ni Line

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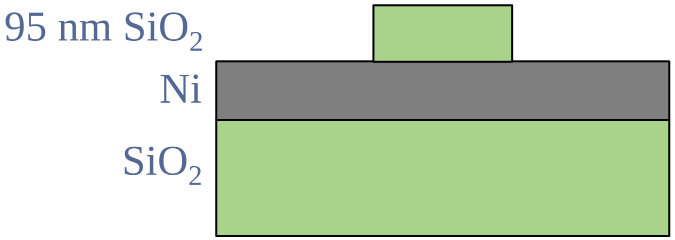
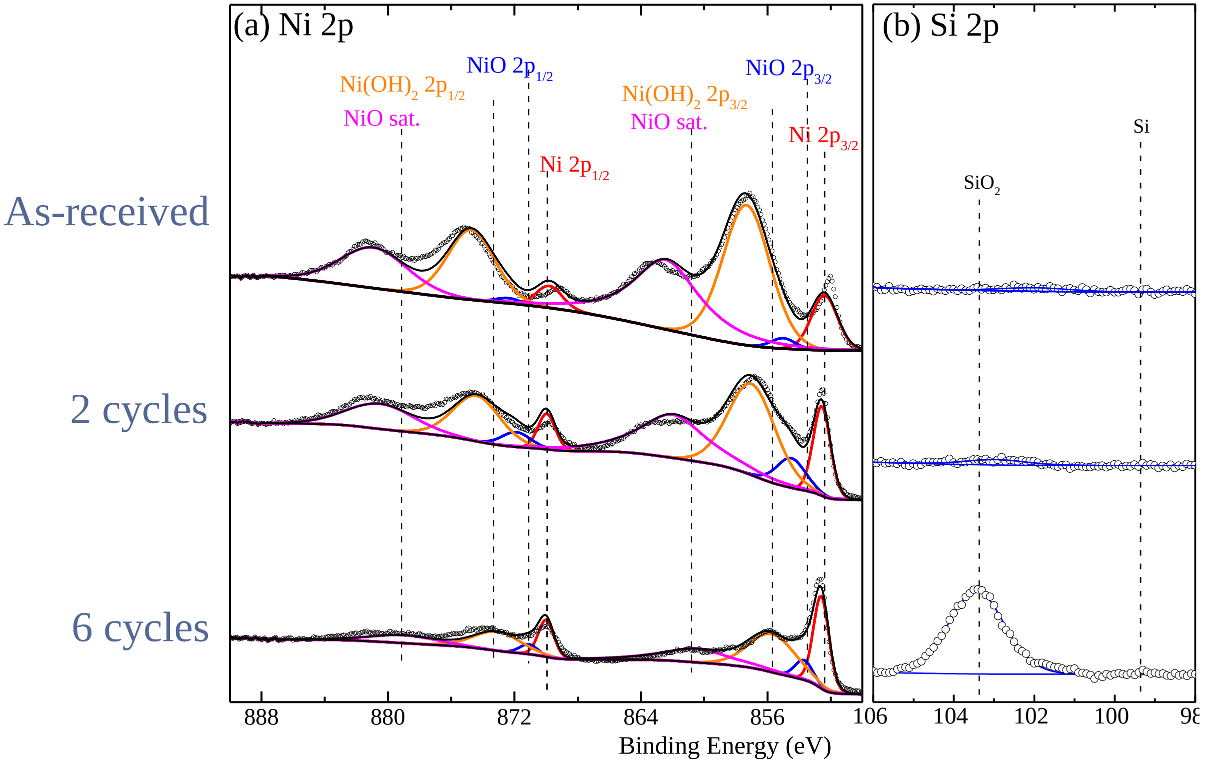
FA	80	NA	NA	350	60



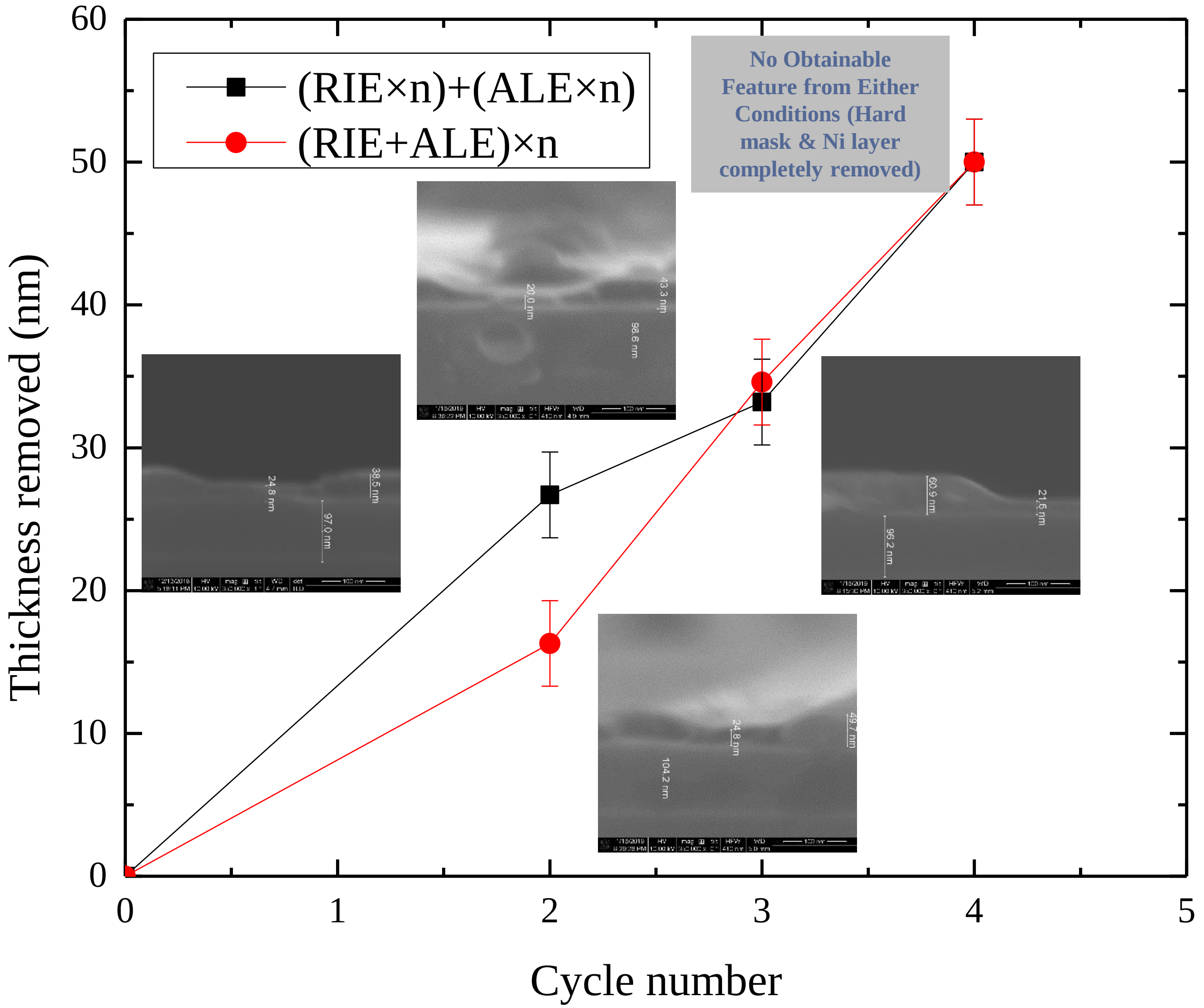


$$\Delta E_{Ni-Ni(OH)_2} \sim 6\ eV$$

$$\Delta E_{Ni-Ni(OH)_2} = 4\ eV$$

- Reduction of Ni signal confirmed chemical removal of Ni
- Oxidation-organic acid exposure has negligible effect on SiO_2

Hybrid Ni RIE/ALE Process



No Obtainable Feature from Either Conditions (Hard mask & Ni layer completely removed)

- Similar linear etch rate observed with both processes
- To be repeated on samples with isolated lines (more vertical sidewall)

Summary

- Thermodynamic calculations suggest that formic acid and acetic acid should be able to etch Ni and NiO in solution phase, formic acid should be able to etch Ni and NiO in vapor phase.
- Etching of Ni was tested at 80ºC using organic solutions: formic acid, acetic acid, acetylacetone (ACAC), and hexafluoroacetylacetone (HFAC). Among which, formic acid and acetic acid showed etching capability.
- Etching of Ni was confirmed on both blanket & patterned (trench & isolated line) samples, sidewall angles quantified on isolated line samples.
- RIE & ALE hybrid process tested on trench samples, better sidewall quantification to be performed on isolated line samples.

Acknowledgement

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  - Semiconductor Research Corporation (SRC)
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- Sample Preparation:
  - Intel Corporation: Dr. Changju Choi, Dr. Guojing Zhang, Dr. Cheng-hsin Ma, Dr. Tristan Tronic, Dr. Cen Tan and Dr. Charles Mokhtarzadeh

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