Plasma Processing of New Materials

May 3, 2022
Online Low Temperature Plasma Seminar

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Outline

- **Plasma processing opportunities and challenges**
- Atomic scale processing of metals and metal oxides
- Plasma assisted deposition
  - Composition control for enhanced functionality
  - Conformality for integration
  - Multilayer architecture to combine complementary properties
- Plasma assisted patterning
  - Specificity with controlled surface chemical states
  - Selectivity from controlled surface reaction
  - Anisotropy from directional ions
- Summary

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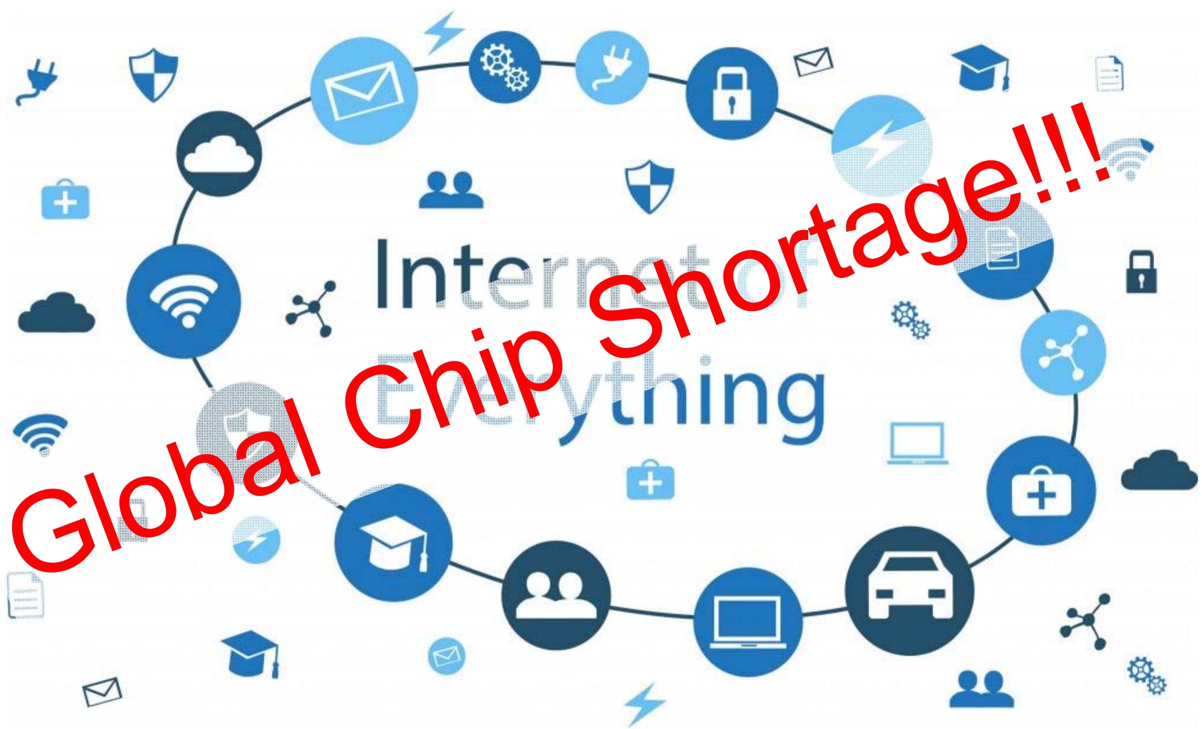
Internet – Redefined by the Pandemic



- Technology enables global connectivity in unprecedented ways, requiring infrastructure

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CHIPS

Creating Helpful Incentives to Produce Semiconductors (CHIPS) for America Act, 2021

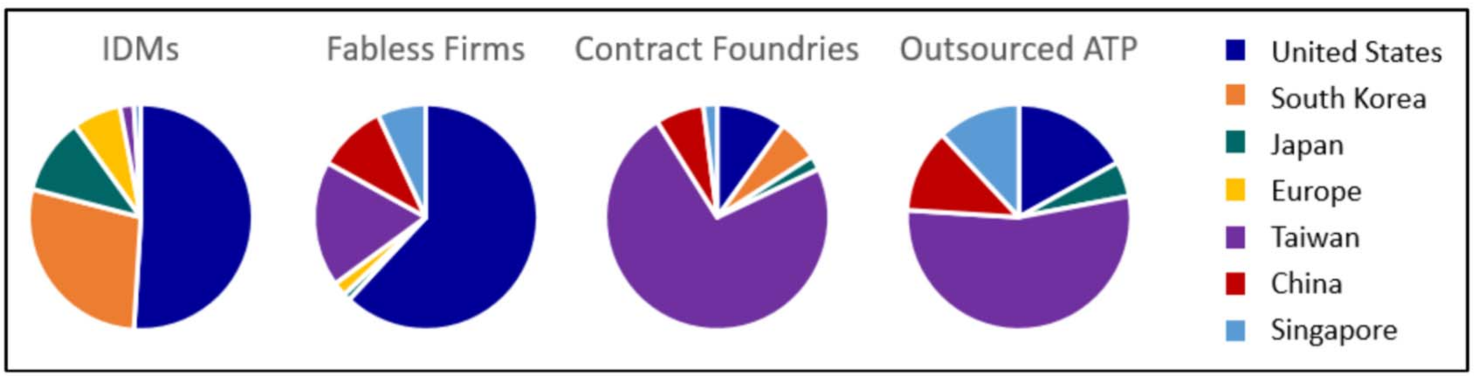
Congressional Research Service
Informing the legislative debate since 1914

Semiconductors: U.S. Industry, Global Competition, and Federal Policy

October 26, 2020

CHemically Integrated Processing for Semiconductors (CHIPS)

Figure 8. Revenue for Value Chain Segments by Headquarters Location, 2018



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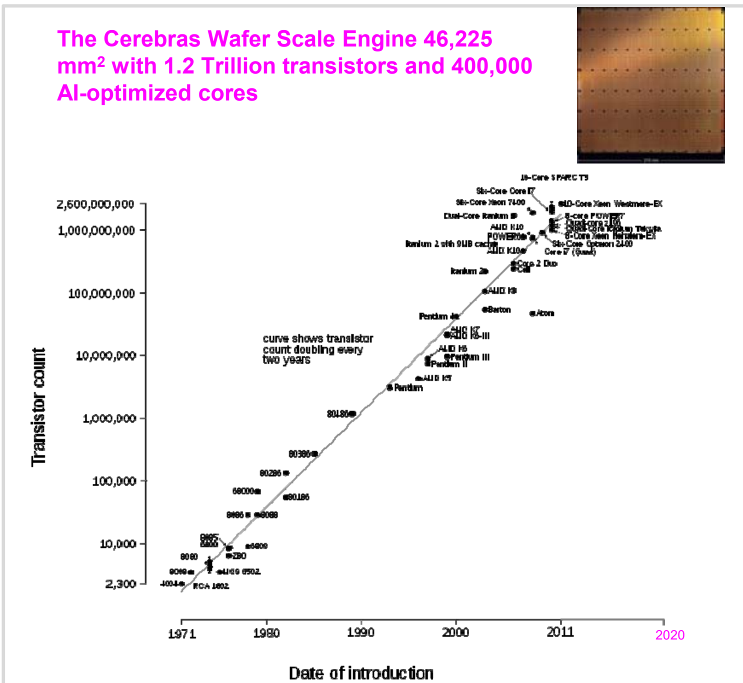
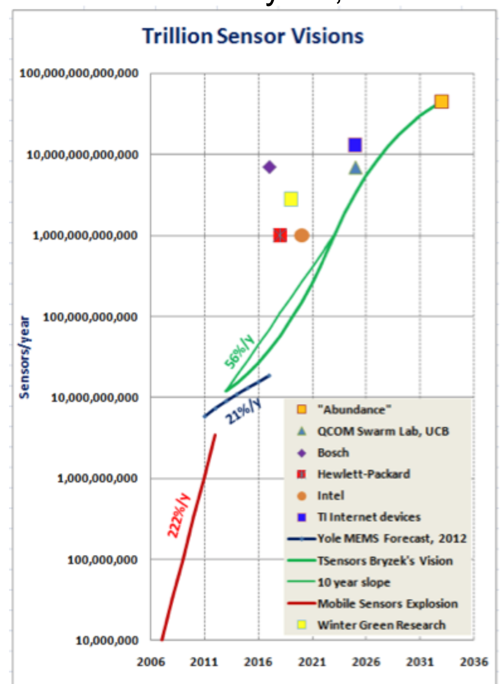
The Era of Trillions

Adapted from Transistor Counts 1971-2011



Janusz Bryzek, 2014



- Someone has to make these trillions of devices
- Emerging technologies rely on **Atomic Layer Processes** (ALP)

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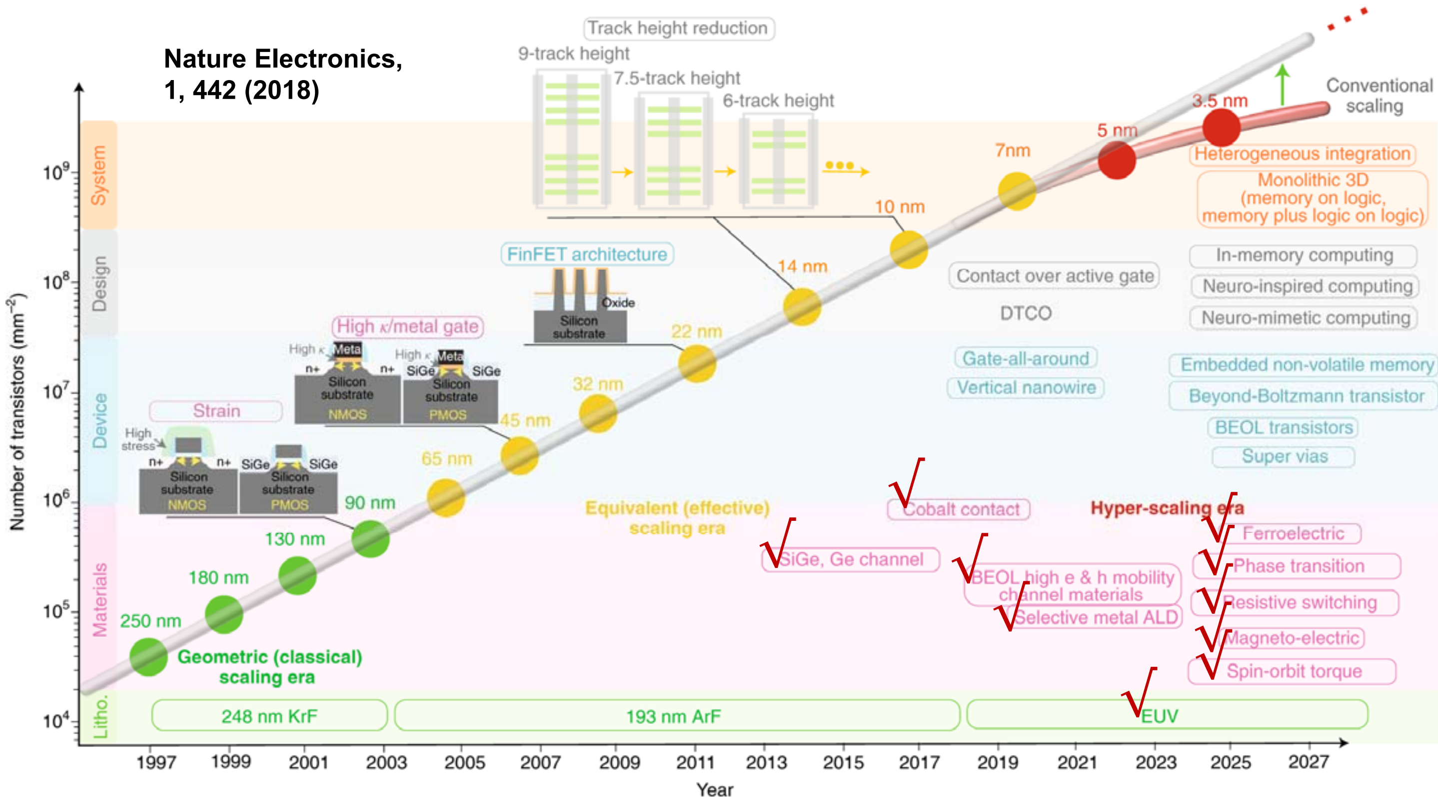
The Era of Scaling



- Multifunctional materials are enablers many critical areas

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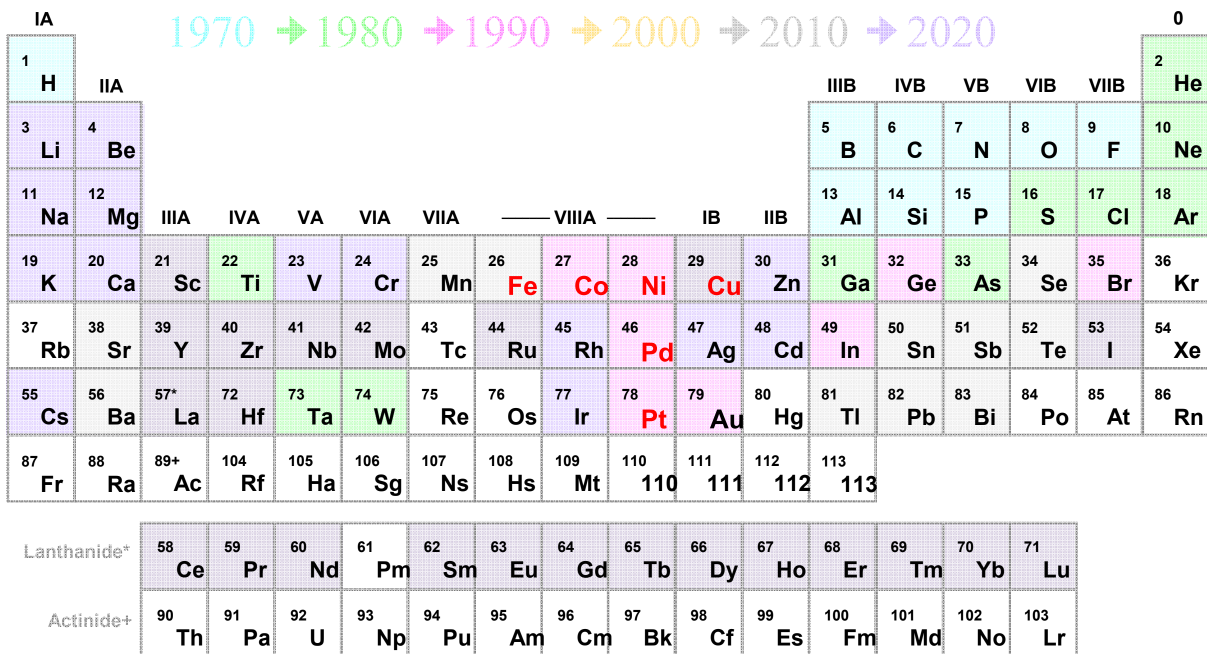
The Era of Metals



- It is much harder to deposit conformally and to etch metals
- How can we realize atomic scale precision in materials processing?

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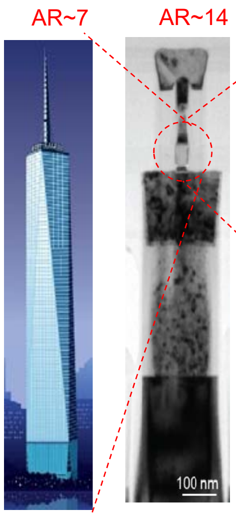
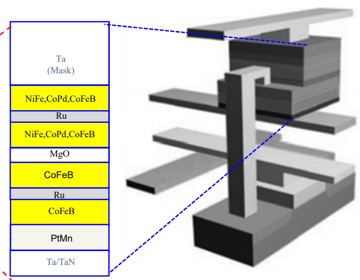
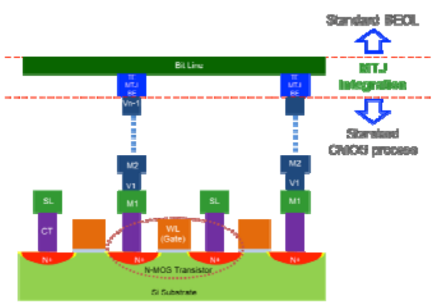
The Era of Challenging Architectures



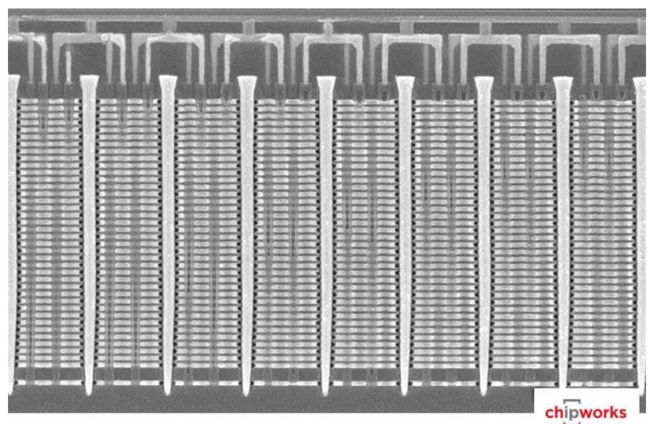
Computer **46**(8): 30-36 (2013)



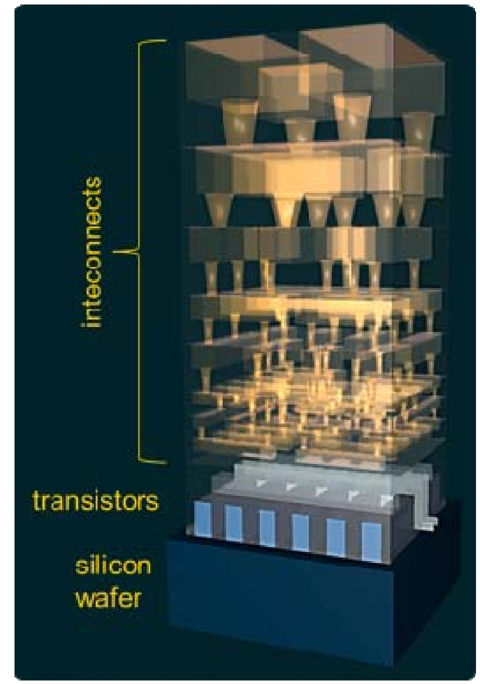
(Magnetoresistive random-access memory)



Device shrinkage + stacking, resulting in extremely high aspect ratio (HAR) features (AR>100)



Close-up image of V-NAND flash array



- Intrinsic material properties (less volatility) and structural complexity (3D, high AR)
- Synthesis and pattering of novel and multifunctional materials (**ALD** and **ALE**)

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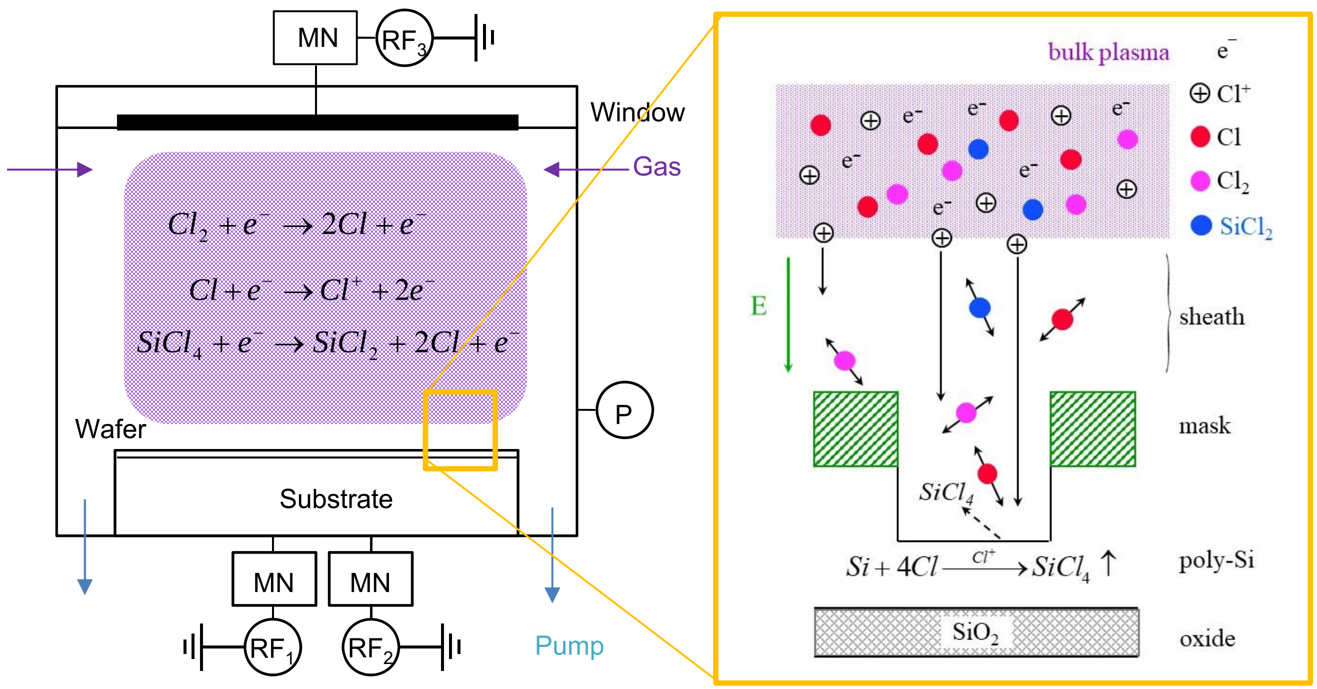
Surface Reactions Driven by n/+



- Ions
  - Chemistry
  - Energy (directional)
  - Angle
- Radicals
  - Chemistry
  - Reactivity (isotropic)
- Synergy
  or individual effect?

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Challenges and Opportunities

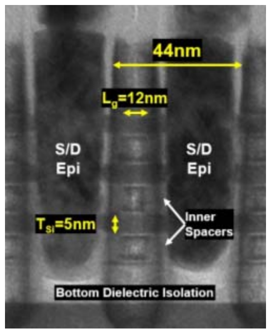
A Single Transistor

→Binary code

→Atomic scale

→Smaller is faster

→Reliability issue



Novel Materials with Atomic Precision

→Two site-specific self-limiting half reactions

→Atomic scale controllability

→Tailored composition and engineered interface

→Highly conformal deposition over 3-D features

- **Composition**
- **Conformality**
- **Multilayer**

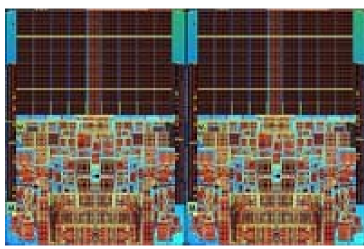
A Tillion Transistors

→Integration

→Pattern fidelity

→Reaction selectivity

→Reliability issue



Nano-scale Patterning

→Compatibility with IC manufacturing

→Highly direction ions for pattern fidelity

→Controlled ion energy, type and ratio to radicals

→Integration with wet surface chemistry

- **Specificity**
- **Selectivity**
- **Anisotropy**

- Plasma based processes are critical in enabling the device integration

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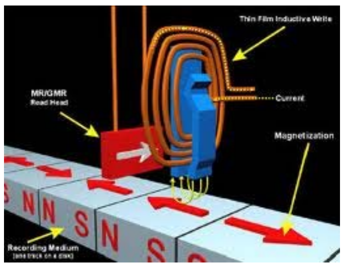
Multiferroics for Electro-Magnetic Devices

EM devices are ubiquitous throughout our society

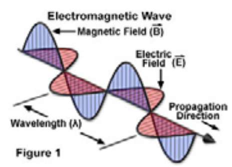
Memory



Energy efficiency

+

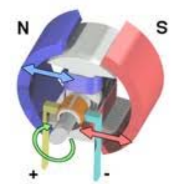
Antenna



Size reduction

+

EM Motor

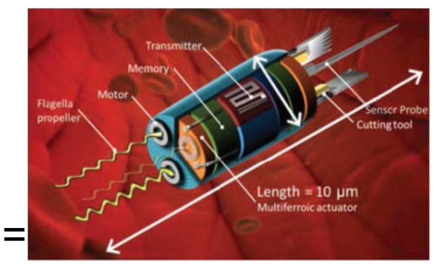


Power increase

=

Turing science fiction into reality

MRS Bulletin, 43, 822 (2018)



Antenna size scales with the wavelength → How do we reduce the size?

Nano-scale multiferroics

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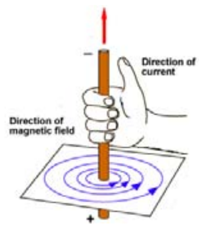
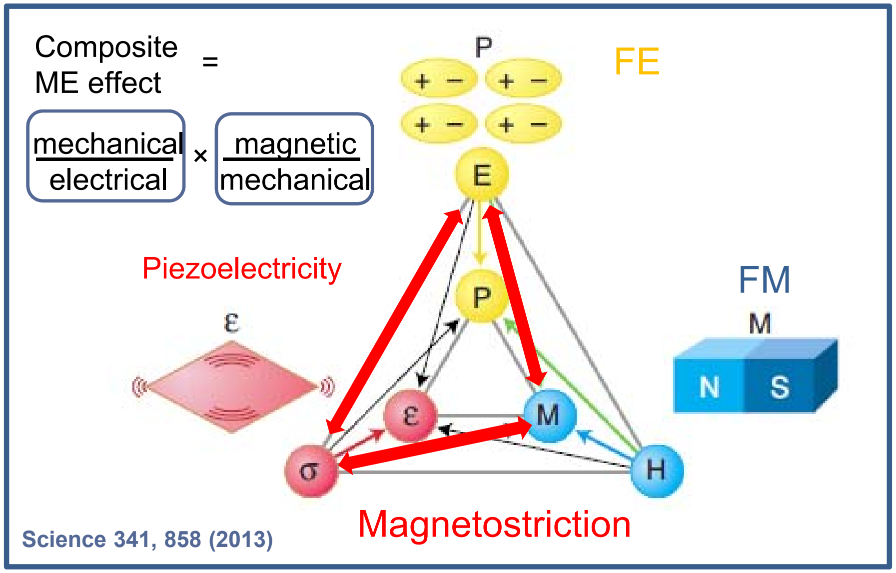
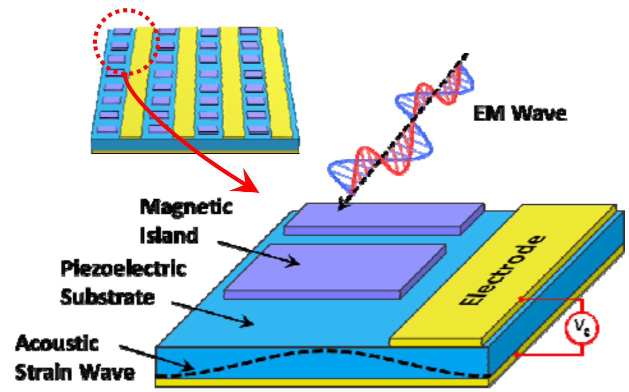
Voltage Control of Magnetism

- EM devices rely on current through a coil to create magnetic fields
  → This approach suffers resistive losses in the small scale
- Designer materials intrinsically create magnetic fields
  → Multiferroic or magnetoelectrics







→5 order of magnitude reduction in size *with the optimal magnetic material*

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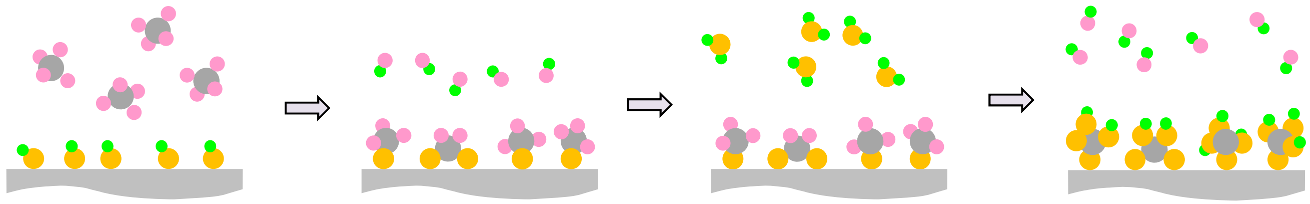
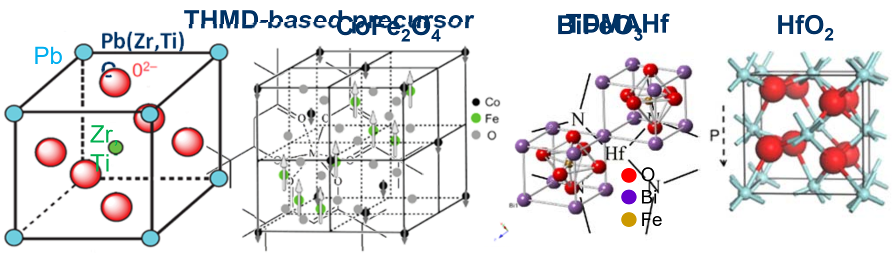
Radical-enhanced ALD for Multiferroics



→**Conformal**, **high-quality** material growth over **large area**

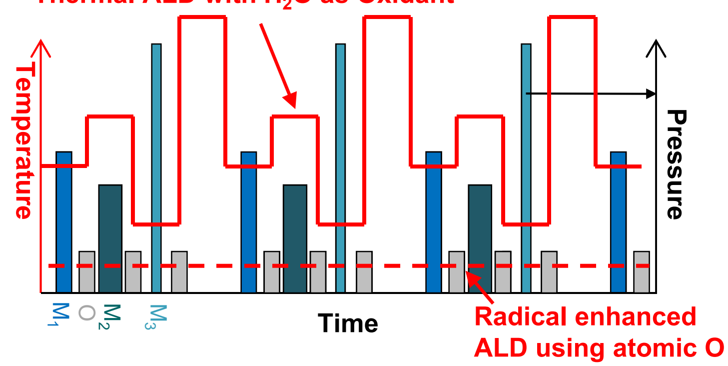
Materials of Interest



M = Bi, Fe, Co. Pb, Zr, Ti, Hf

→ Need of **low-temp** processing

Radical Enhanced ALD



- PEALD can realize the synthesis of complex oxides at **low temperatures**

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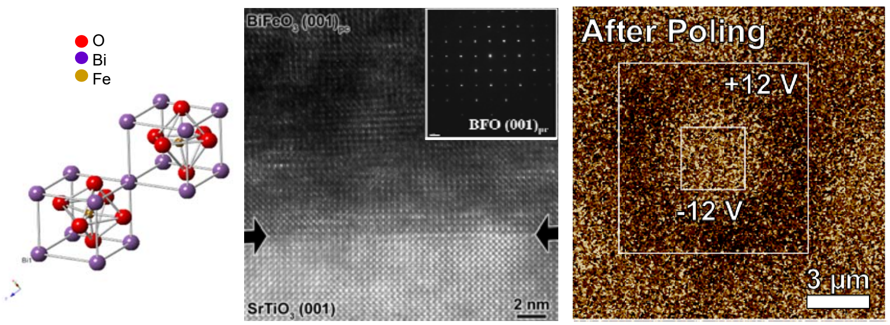
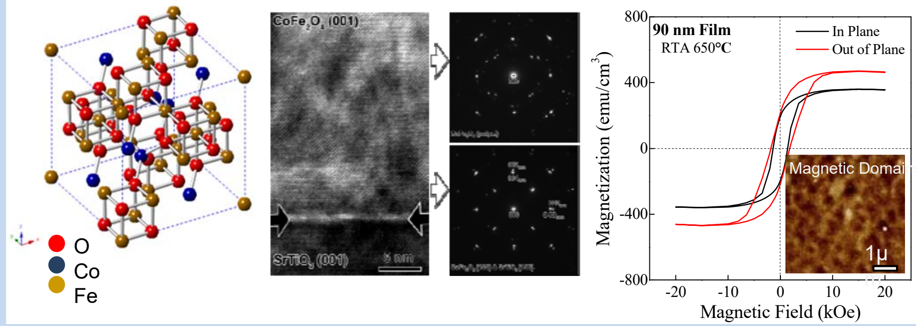
Multiferroic Composites Design

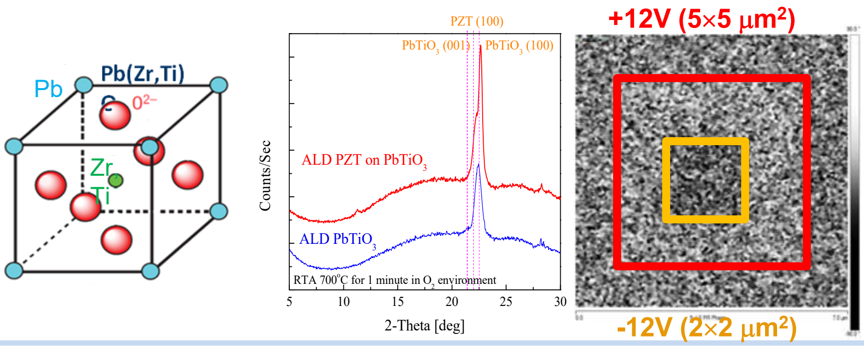
Multiferroic Perovskite $BiFeO_3$



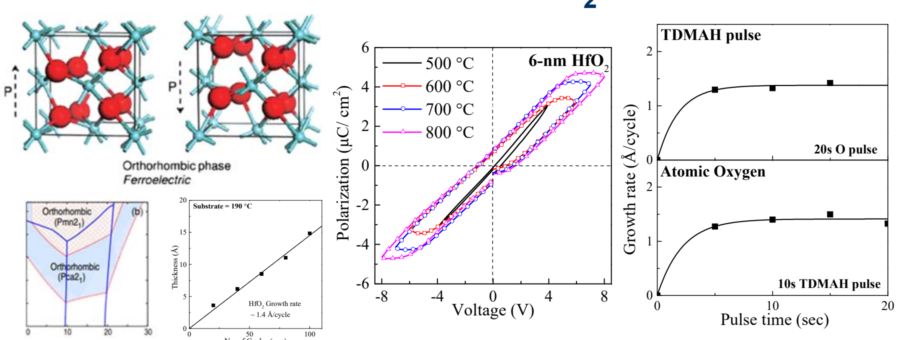
Ferrimagnetic Spinel $CoFe_2O_4$



Piezoelectric PZT (thermal ALD)



Ferroelectric Orthorhombic HfO_2



- Composition control is achieved by RE-ALD, thereby tailoring the desired ferroic properties

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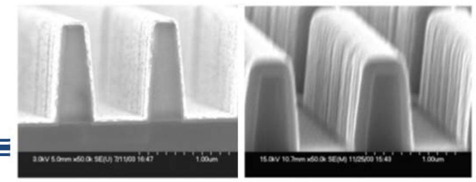
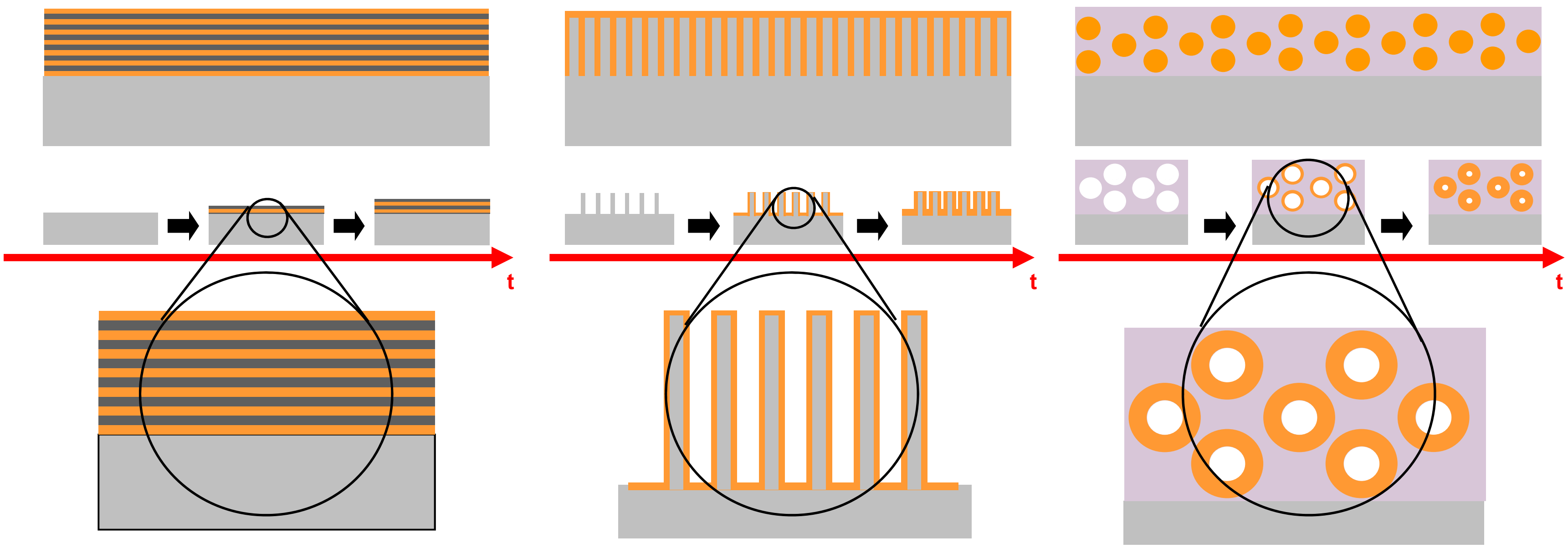
RE-ALD Enabled Multiferroics



Nanostructured Composites can improve magnetoelectric coupling



2D-2D
ALD multilayers

1D-3D
ALD over MEMS features

0D-3D
ALD over porous structures

- Highly conformal ALD coating over non-planar surfaces, mesoporous materials
- Need nanosystems with controlled architecture

[1] He H C et al., 2009, J. Phys. D:Appl. Phys. **42**, 095008 [2] Wan J G et al., 2005 Appl. Phys. Lett. **86**, 122501 [3] Wan J G et al., 2006, Appl. Phys. Lett. **89**, 122914

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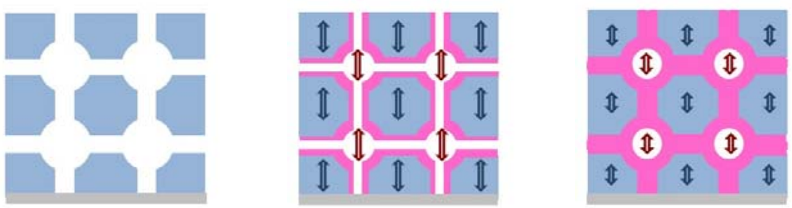
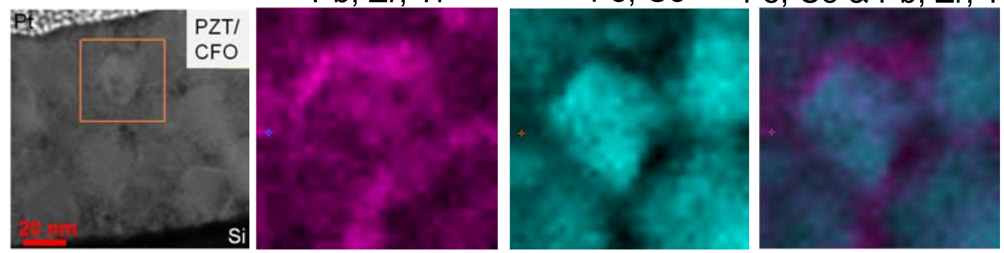
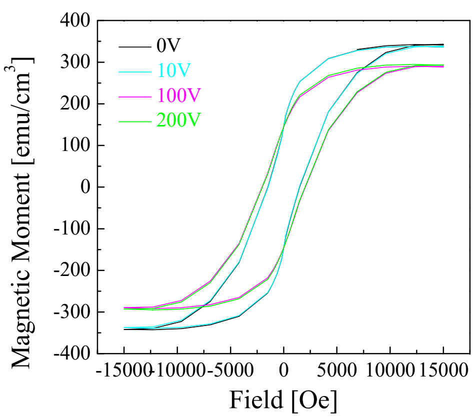
Strain Transfer in 0D-3D CFO-PZT

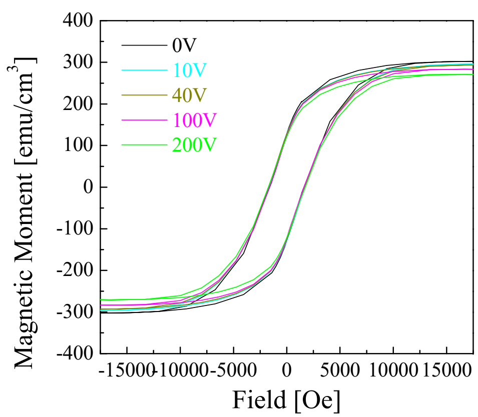
Mesoporous CFO | **3 nm thermal ALD PZT** | **6 nm thermal ALD PZT**

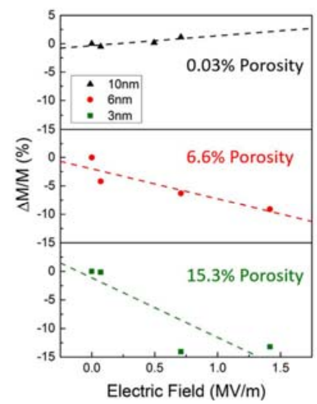


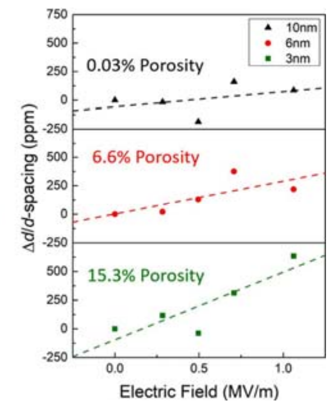
EDS | Pb, Zr, Ti | Fe, Co | Fe, Co & Pb, Zr, Ti











- Conformality and tailored porosity enhances strain transfer at the interface
- In 3-D porous films, RE-ALD has limited conformality compared to thermal ALD

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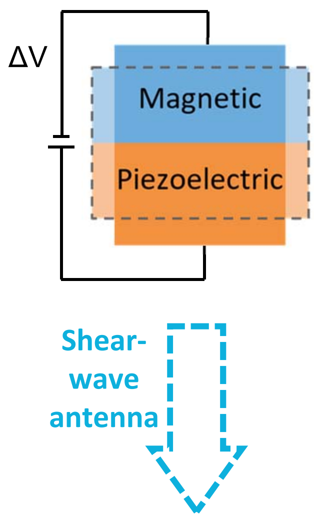
Bottleneck – Soft Magnetostrictives



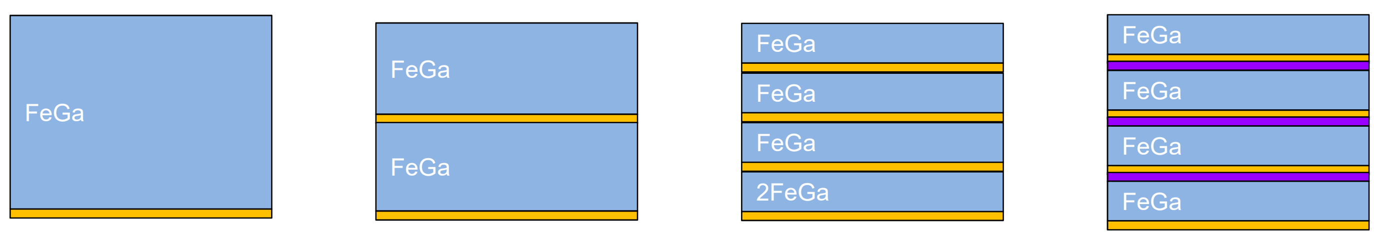
$$\lambda_{AW} = \frac{v_{substrate}}{f_{EM}} \approx 10^{-5}\,\lambda_{EM}$$

Material	H_c (Oe)	FMR LW (Oe)	λ_s (ppm)	$d\lambda/dH$ (ppm/Oe)
Ni	35	~180	41	0.17
$Tb_xDy_{1-x}Fe_2$	2300	~1200	880	2.8
$Ni_{80}Fe_{20}$	<3	30	<3	0.01
$Fe_{80}Ga_{20}$	65	260	~200	~1

- Conventionally, there is a trade-off between soft magnetic properties and high magnetostriction

How to enhance soft magnetic properties of magnetostrictive FeGa?

1. **Underlayer (NiFe)** tailors microstructure
2. **Multilayering** maximizes magnetic softness **(N)**
3. **ALD Al_2O_3** reduces eddy current loss



- Underlayer can influence film microstructure and grain size
- Plasma based thin film processing (PVD) tailors microstructure and interfacial stress

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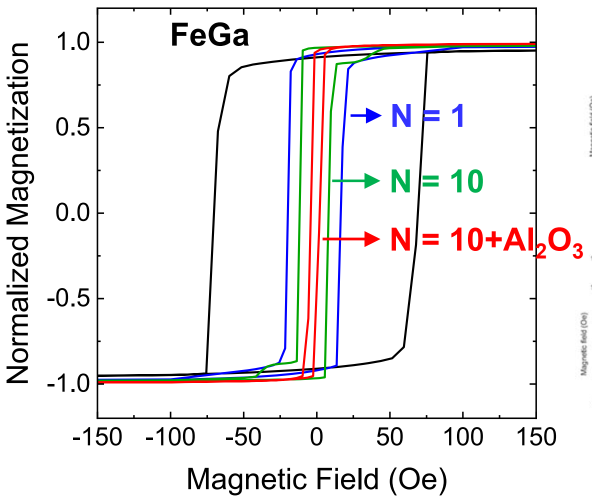
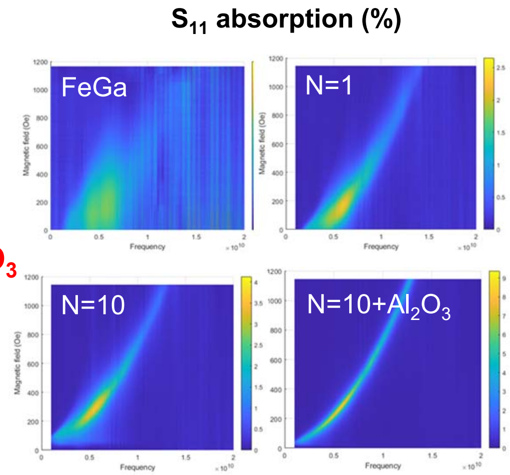
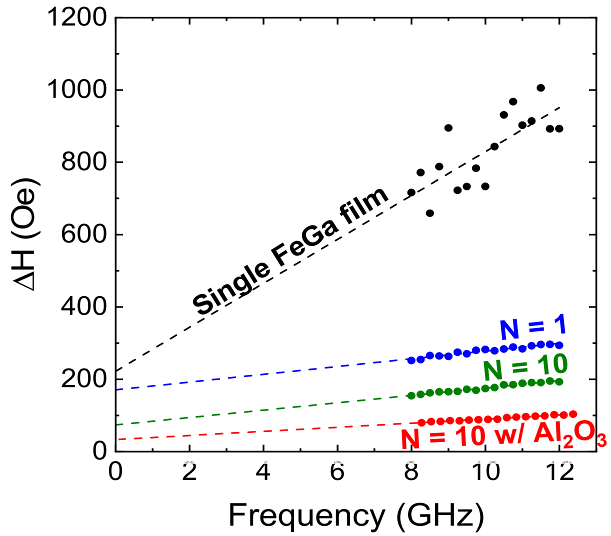
Multilayer with Enhanced Performance







Sample	Gilbert damping (α)	ΔH_0 (Oe)
Single FeGa film	0.0851 ± 0.0190	225 ± 137
N = 1	0.0143 ± 0.0012	171 ± 8
N = 10	0.0143 ± 0.0006	73 ± 4
N = 10 w/ Al_2O_3	0.0081 ± 0.0003	38 ± 2

error reported to ± 1 σ

Material	H_c (Oe)	FMR LW (Oe)	λ_s (ppm)	dλ/dH (ppm/Oe)
$Ni_{80}Fe_{20}$	<3	30	<3	0.01
$Fe_{80}Ga_{20}$	65	260	~200	~1
FeGa/NiFe (N=5)	7	18	~200	~8

- Plasma processing combined complementary properties to enable giant magnetostriction and low loss in designed multilayers

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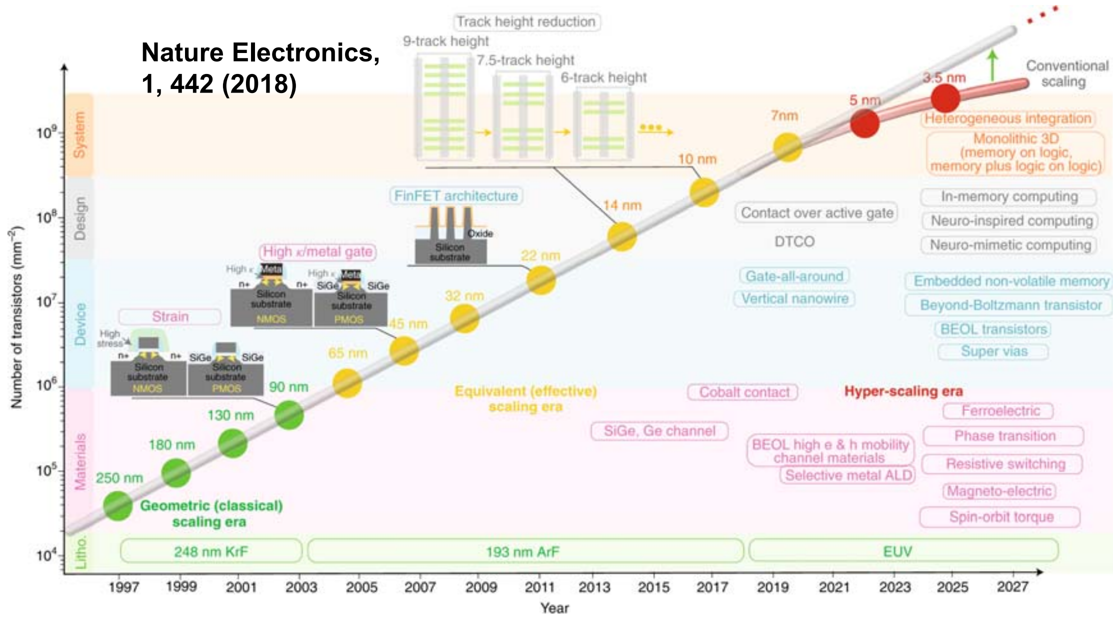
Etch: Universal ChemicaL Approach (UCLA)?



Nature Electronics, 1, 442 (2018)

How can we realize atomic scale precision with etching specificity, selectivity, and directionality (w/o halogen)?

1. **Thermodynamics** to evaluate feasible reactions
2. **Kinetically** modifies the surface to achieve chemical contrast
3. **Low energy ions** to control anisotropy

Materials needed:

- Ferroelectric
- Magnetic
- Magneto-electric
- Phase change

Elements involved:

- O, Hf, Co, Fe, W, Pt, Pb, Zr, Ti, Al, Nb, Ge, Sb, Te, In, Ga, Zn, Cu

→ **Metal alloys**

→ **Metal oxides**

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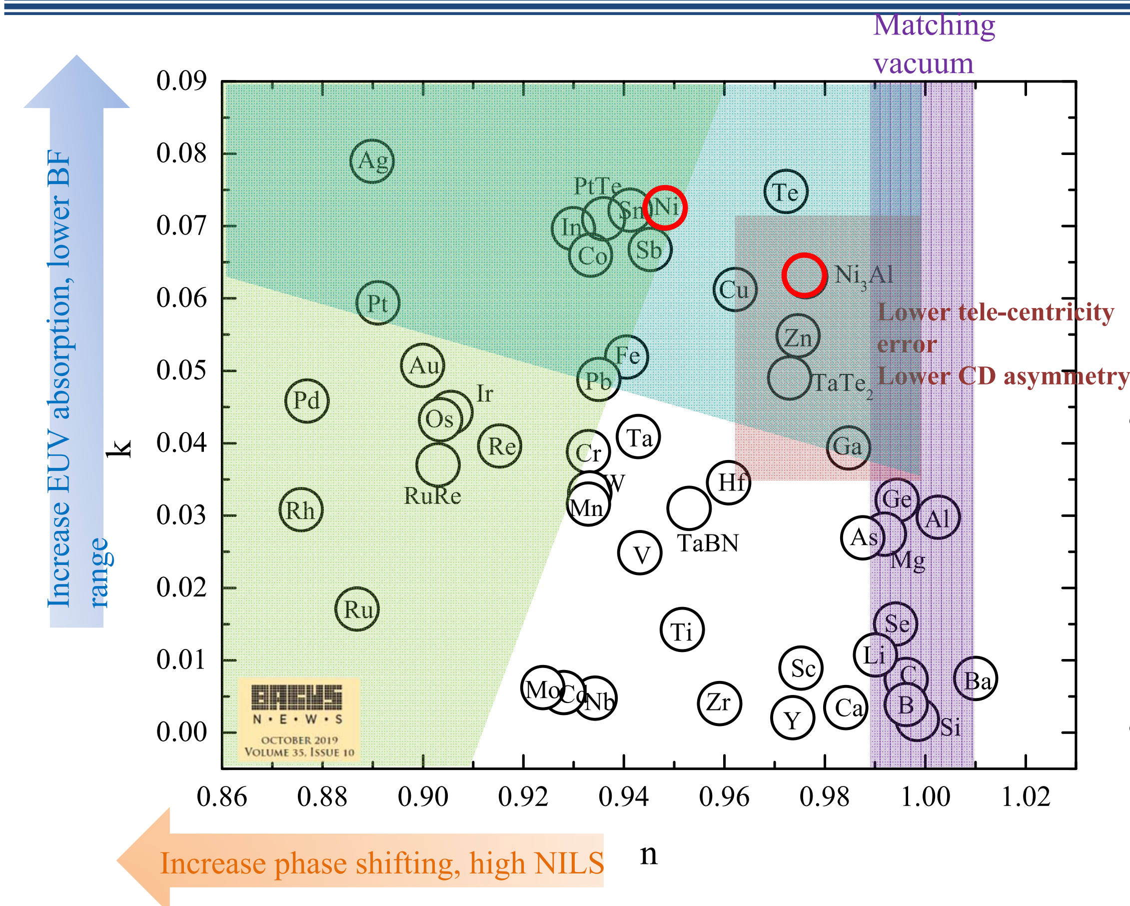
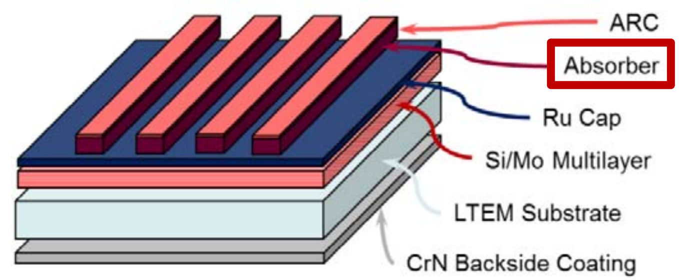
Patterning EUV Absorber (model system)





- EUV (13.5 nm) = reflection instead of transmission
  - Much more costly
  - Much strict environment (vacuum)
  - New mask design needed
  - New manufacturing constraints
- **Ni as a model system but more complex materials needed**

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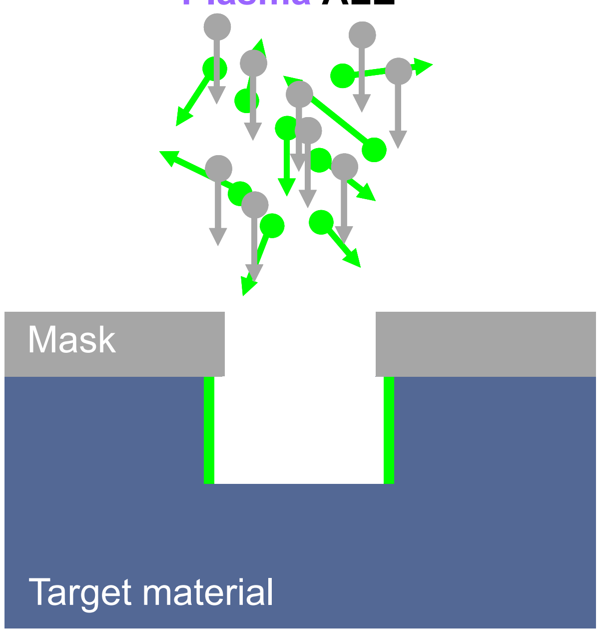
Strategies for Atomic Layer Etching

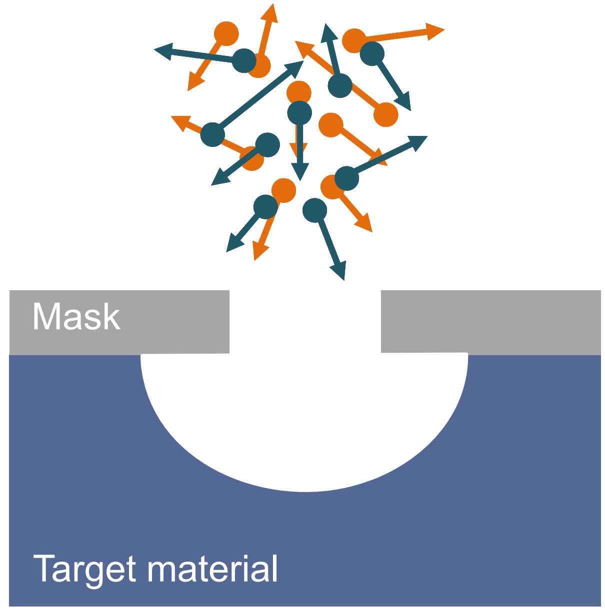
Plasma ALE



$$M-M-M_{(s)} + X/X^{+} \rightarrow M-M-MX_{(s)}$$

$$M-M-MX_{(s)} \xrightarrow{Ar^{+}} M-M_{(s)} + \mathbf{MX}_{(g)}$$

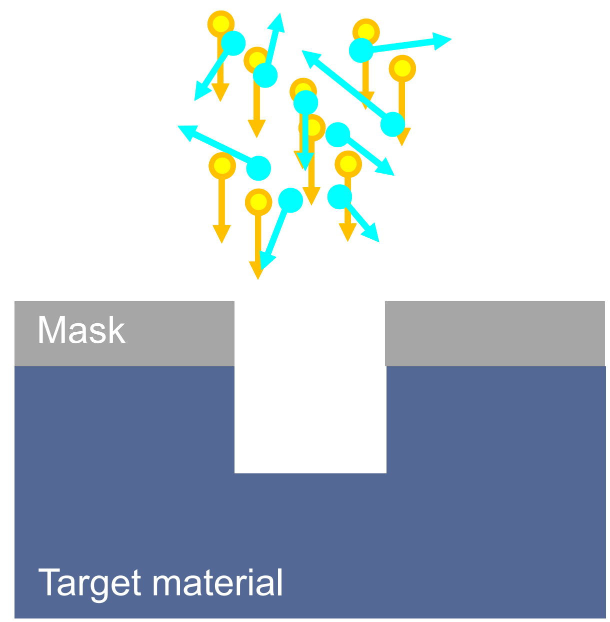
Thermal ALE



$$M-M-M_{(s)} + X/X^{+} \rightarrow M-M-MX_{(s)}$$

$$M-M-MX_{(s)} + RX_{(g)}$$
$$\rightarrow M-M_{(s)} + \mathbf{RX-M-X}_{(g)}$$

Plasma-Thermal ALE



$$M-M-M_{(s)} + X^{(+)}{}_{(g)} \rightarrow M-M-MX_{(s)}$$

$$M-M-MX_{(s)} + Y_{(g)} \rightarrow M-M_{(s)} + \mathbf{MXY}_{(g)}$$

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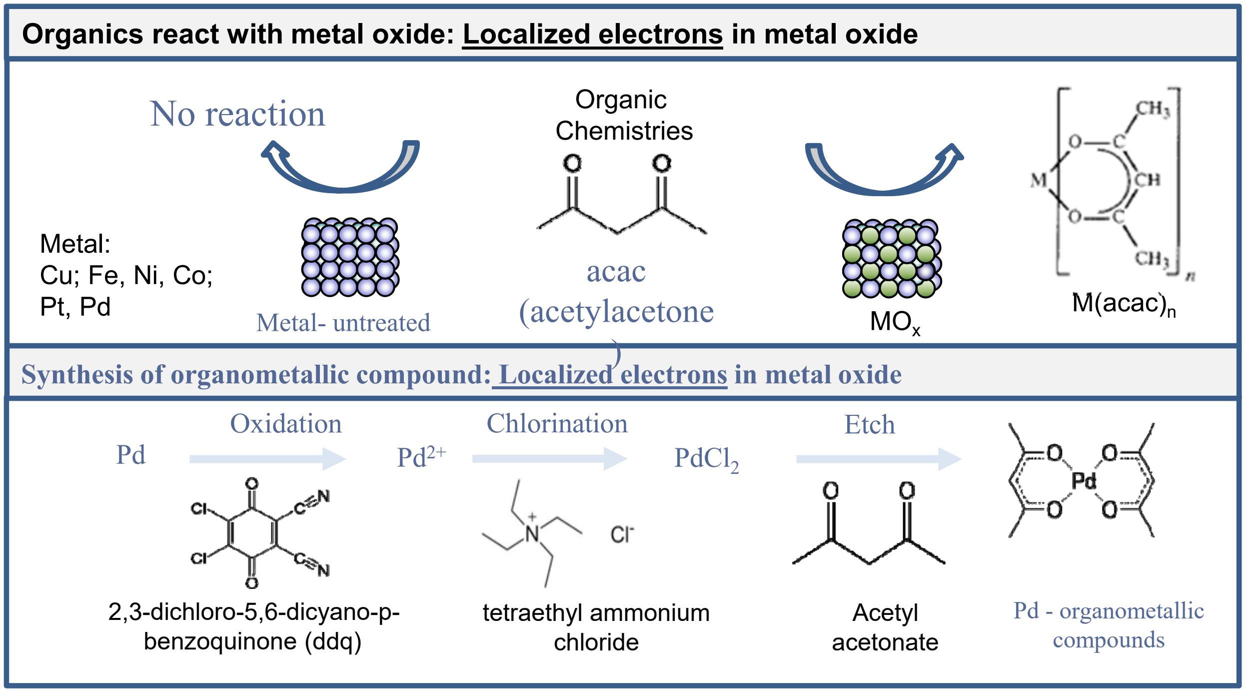
Importance of Surface State

Organometallic etch for **metals** (many of metals have organic precursor for ALD)



- Surface modification is necessary to facilitate metal etch with organics

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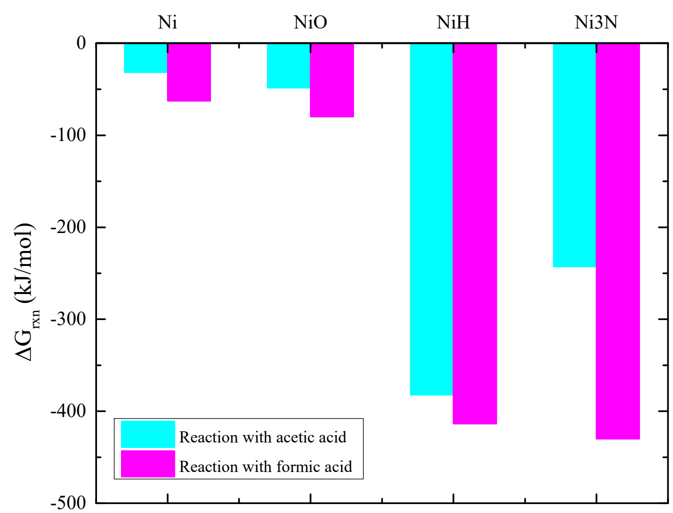
D. W. Hess et al ECS 142 (1995) 961; R. I. Masel et al. JVST A. 16 (1998) 3259; S.W. Kang et al. JVST B. 17 (1999) 154

Assessment of Ni-compound*

- Lower ΔG for NiO suggest oxidation would promote reactions with acids
- Solution phase etching ER≈ 1.5 nm/min for Ni in formic acid and ER≈ 45 nm/min for NiO in formic acid with reaction products (nickel formate) measured



	Acetic acid		Formic acid	
	Reaction	ΔG_{rxn} (kJ/mol)	Reaction	ΔG_{rxn} (kJ/mol)
Ni	$Ni(s)+2CH_3COOH(g) \rightarrow Ni(CH_3COO)2(aq)+H_2(g)$	-31.48	$Ni(s)+2HCOOH(g) \rightarrow Ni(HCOO)2(aq)+H_2(g)$	-62.7
NiO	$NiO(s)+2CH_3COOH(g) \rightarrow Ni(CH_3COO)2(aq)+H_2O(g)$	-48.48	$NiO(s)+2HCOOH(g) \rightarrow Ni(HCOO)2(aq)+H_2O(g)$	-79.7
NiH	$NiH(g)+2CH_3COOH(g) \rightarrow Ni(CH_3COO)2(aq)+1.5H_2(g)$	-382.22	$NiH(g)+2HCOOH(g) \rightarrow Ni(HCOO)2(aq)+1.5H_2(g)$	-413.44
Ni_3N	$2Ni_3N(s)+12CH_3COOH(g) \rightarrow 6Ni(CH_3COO)2(aq)+N_2(g)+6H_2(g)$	-242.62	$2Ni_3N(s)+12HCOOH(g) \rightarrow 6Ni(HCOO)2(aq)+N_2(g)+6H_2(g)$	-429.97

Calculation done for 25℃, 1 atm. Data from HSC

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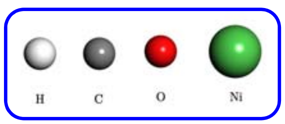
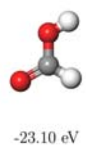
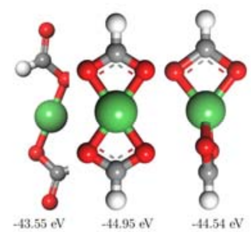
Reaction Product Analysis



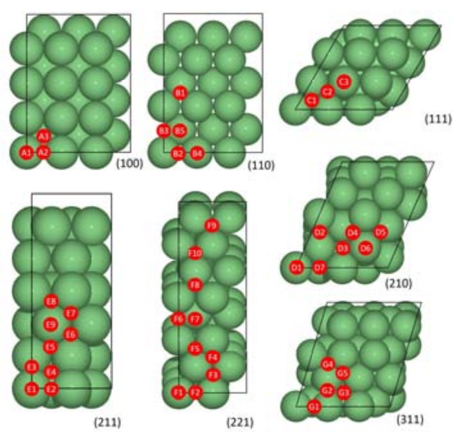




$\cdot NiO + HFA \rightarrow \cdot + [Ni(FA)_2] + H_2O$

$\cdot Ni + 2HFA \rightarrow \cdot + [Ni(FA)_2] + H_2$

$\Delta G_{et} > 0$ eV



$\alpha\{l + 1 , NiO_\theta\} + 2HCOOH$
$\rightarrow \{l, Ni\} + (\alpha\text{-}1)\{l + 1 , Ni\}$
$+ [Ni(HCOO)_2] + H_2O$

$$\Delta G_{ads} = (G_{NiO\theta} - G_{Ni} - n_O\mu_O)\,]/n_O$$
$$\cong (E_{NiO\theta} - E_{Ni} - n_O\mu_O)\,]/n_O$$

Surface	Site	ΔG_{ads} (eV)	Site name
(100)	A1	-0.43	t (top, 1-fold)
	A2	-1.63	b (bridge, 2-fold)
	A3	-2.34	4h (4-fold hollow)
(110)	B1	-1.80	3h (3-fold hollow)
	B2	-1.76	sb (step bridge)
	B3	-1.54	lb
	B4	-0.58	t-p (trough-peak)
	B5	-1.53	t-t
(111)	C1	-2.04	3h-fcc
	C2	-1.92	3f-hcp
	C3	-0.22	t
(210)	D1	-0.70	t-p
	D2	-1.59	b-t
	D3	-1.66	4h
	D4	-1.67	3h-1
	D5	-1.67	3h-2
	D6		t-t
	D7	-2.26	b-p
(211)	E1	-0.59	t-p
	E2	-1.86	b-p
	E3	-1.22	b-cs (counterstep)

Surface	Site	ΔG_{ads} (eV)	Site name
(211)	E4	-1.82	4h
	E5	-1.62	3h-hcp-s-1
	E6	-1.68	3h-hcp-s-2
	E7	-1.92	3h-fcc-s-1
	E8	-2.14	3h-fcc-s-2
	E9		t-s
(221)	F1		t-p
	F2	-1.82	b-p
	F3	-1.84	3h-hcp-s-2
	F4	-1.91	3h-fcc-s-1
	F5	-1.83	3h-hcp-s-1
	F6	-1.56	Lb
	F7	-0.58	t-t
	F8	-2.18	3h-fcc-s-3
	F9	-1.85	3h-hcp-cs
	F10	-1.58	3h-fcc-s-2
(311)	G1	-1.88	b-p
	G2		b-t
	G3	-1.80	4h
	G4	-1.99	3h-hcp
	G5	-1.61	3h-fcc

- The sites are defined by the coordination numbers and the position on the surface

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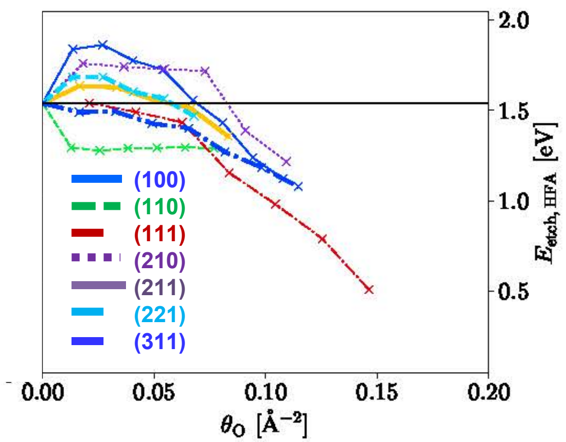
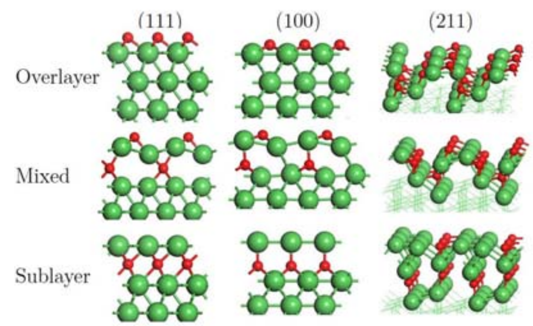
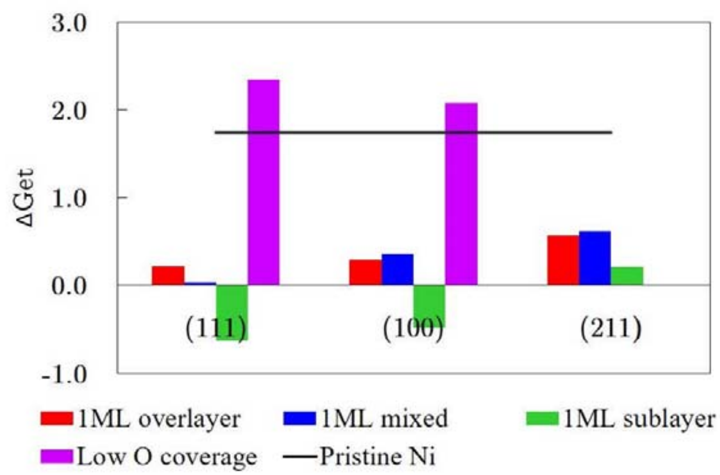
Driving Force for Etching Reactions

Adsorption energy, etching energy of different surfaces vs coverage







- At a high coverage of oxygen, with occupation of subsurface sites and the formation of a surface NiO layer, a favorable etch is observed
- The geometry distortion caused by the oxygen modifier provides a favorable driving force; the difference suggests that site specificity can be important

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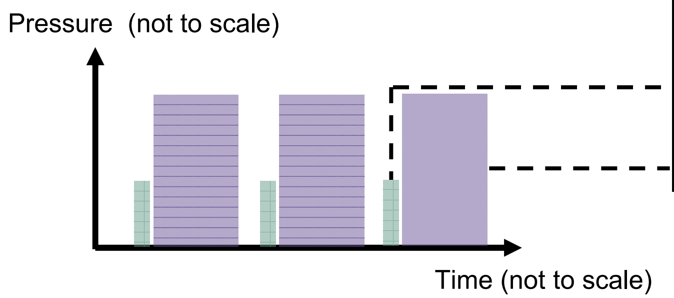
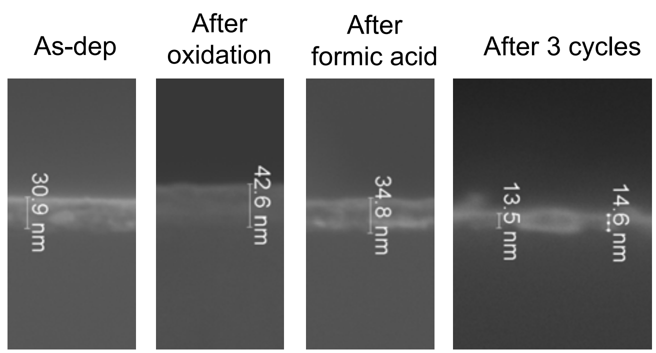
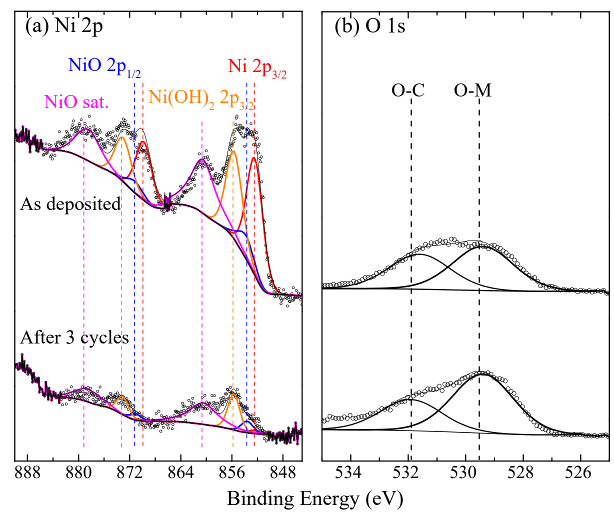
ALE Cyclic Gas Phase Etching of Ni



Chemistry	Pressure (Torr)	Temperature (℃)	Power (W)	Bias (W)	Time (min)
O_2	0.01	25	500	50	2
Vacuum break					5
FA	350	80	NA	NA	60





- Reduction of Ni signal confirmed removal of Ni; etch rate of ~5 nm/cycle
- Selectivity of NiO to Ni in 80℃ formic acid vapor: >100

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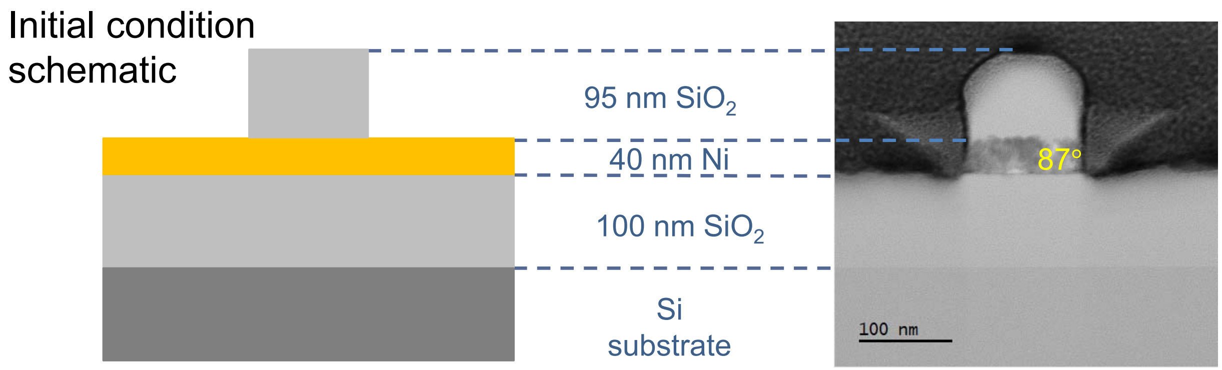
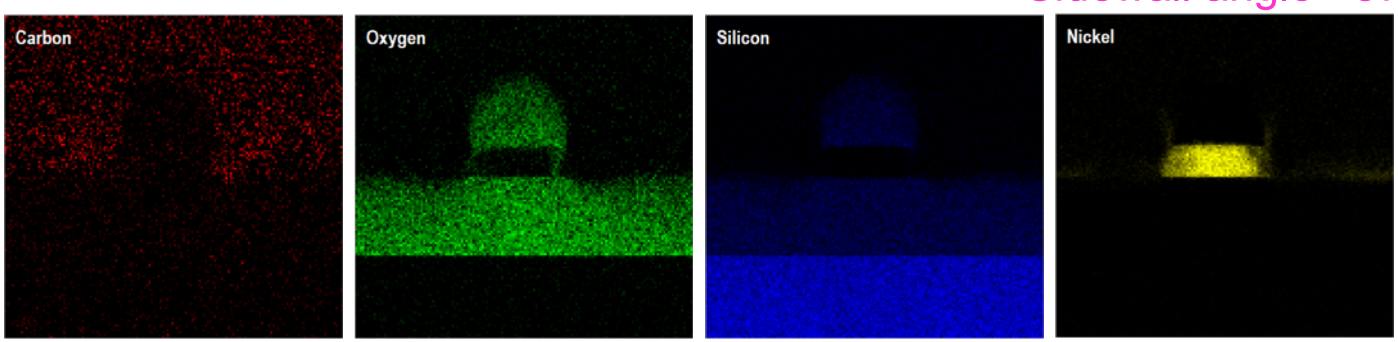
HRTEM of ALE Etched Ni Lines



Sidewall angle ~87°



- Some oxidation of exposed sidewalls was observed
- Elemental mapping confirmed etching of Ni and the etching anisotropy

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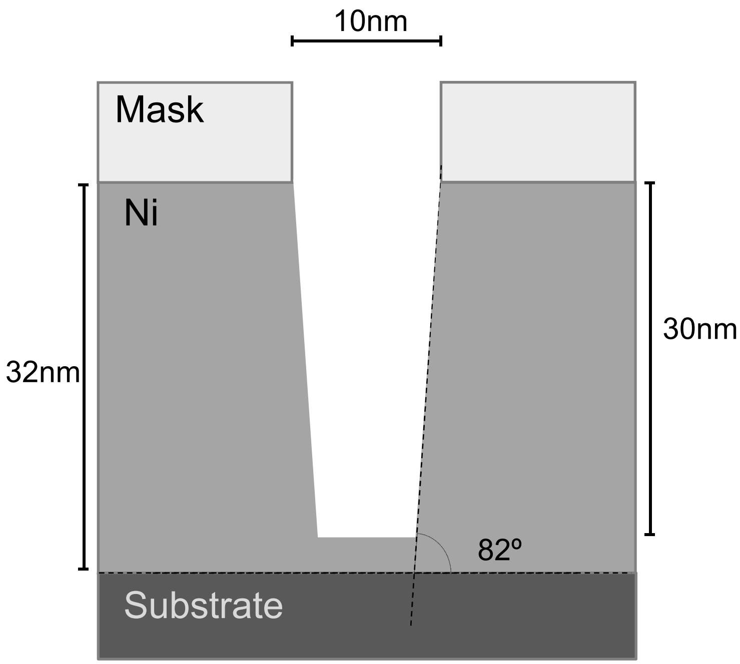
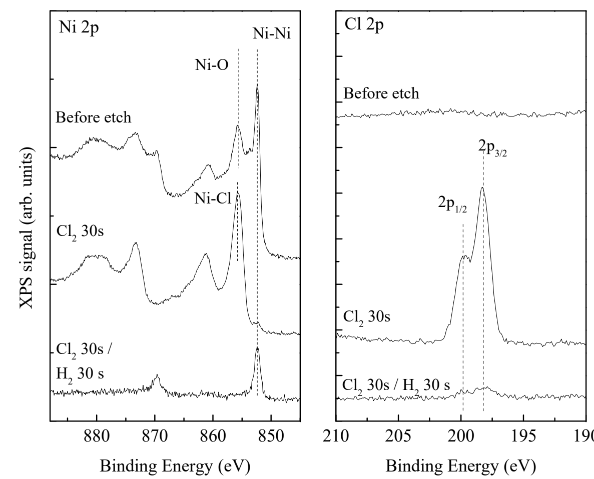
Hybrid Ni RIE/ALE Process



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

Cl_2	500W_s	30s
H_2	-100V_b	30s

XPS of Ni thin film after Cl_2 & H_2 plasma exposures



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

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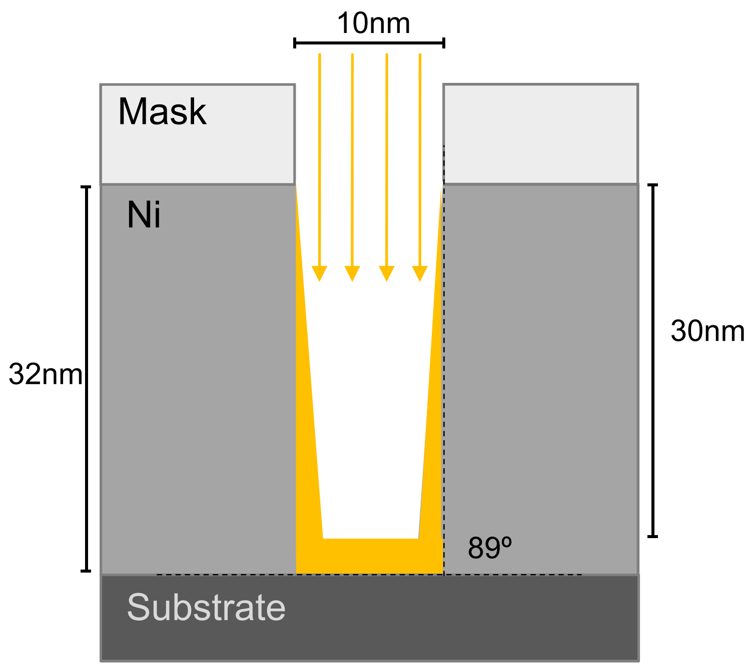
Hybrid Ni RIE/ALE Process



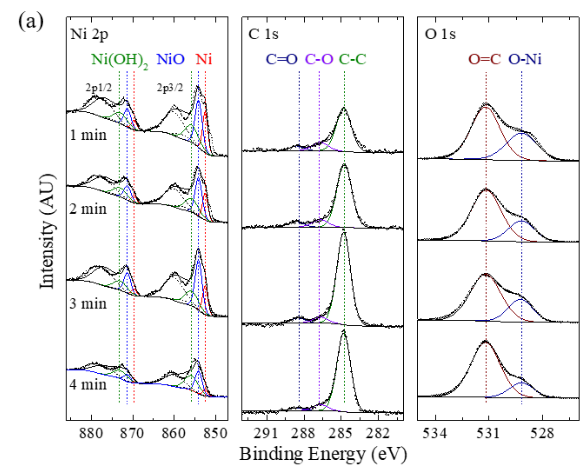
1): Alternating reactive ion etch
Goal: Etch bulk of Ni layer, Θ_{SW}=82°

Cl_2	500W_s	30s
H_2	-100V_b	30s

2) Directional surface modification
Goal: Directionally generate oxide

O_2	500W_s -100V_b	300s

XPS of Ni thin film after different oxidation times



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

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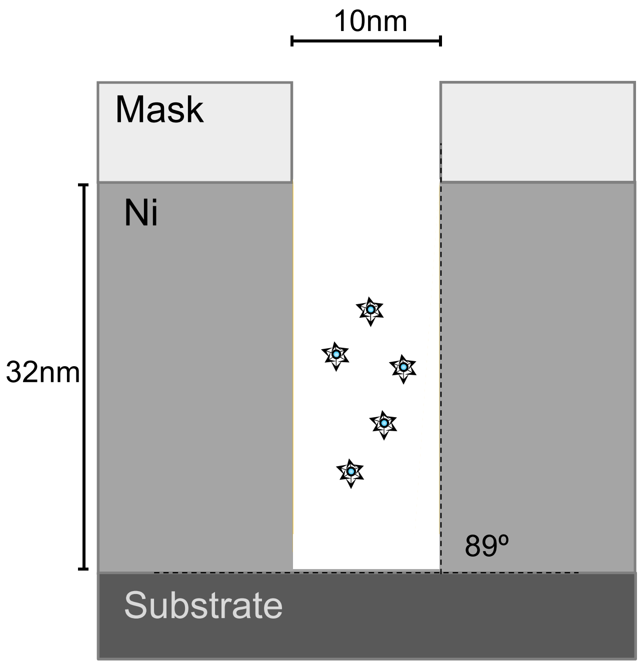
Hybrid Ni RIE/ALE Process



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

Cl_2	500W_s	30s
H_2	-100V_b	30s

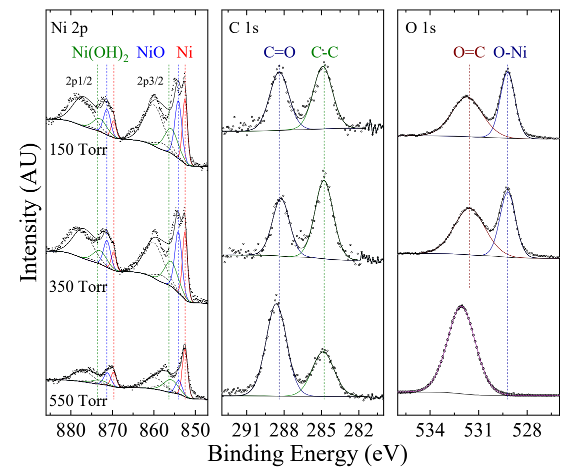
2) Directional surface modification
Goal: Directionally generate oxide

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

XPS of Ni thin film after formic acid exposure at different pressures



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

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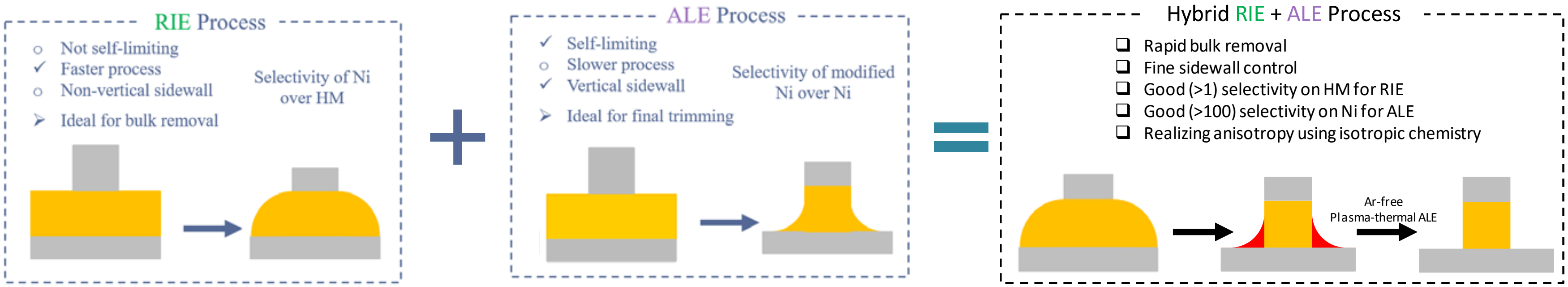
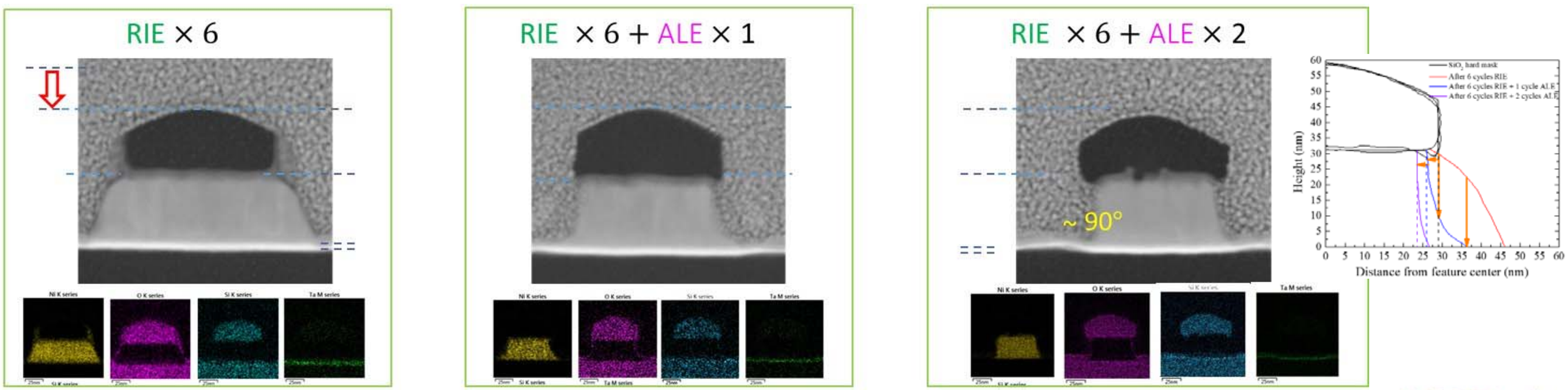
Ni Patterning for EUV Absorbers





- Hybrid RIE + ALE chemistry combines the advantages of both processes

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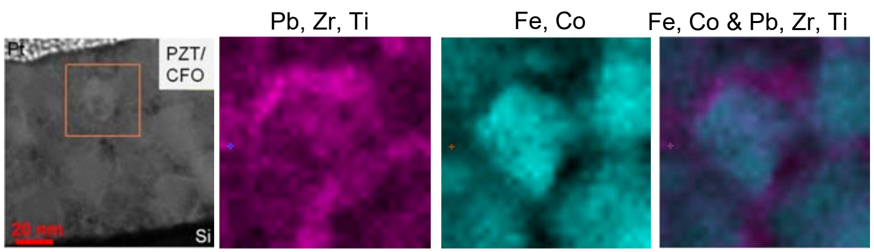
Plasma Enables Atomic layer Processing

ALD



At least one self-limiting reaction

Gas-phase processing, surface reaction

Self-limiting reactions → precision in composition

Surface controlled reaction → limited conformality

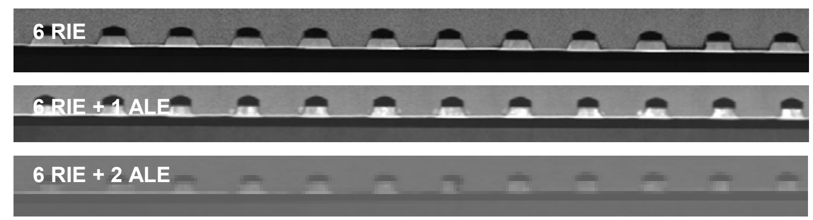
Combining complementary properties → multilayer

Widely used for oxide

Demonstrated for semiconductor

Limited demonstration for metal

ALE



At least one self-limiting reaction

Gas-phase processing, surface reaction

Surface site and state → specificity

Chemical contrast → etching selectivity

Ion energy → etching anisotropy

Demonstrated for oxide

Limited demo for semiconductor

Limited demonstration for metal

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Acknowledgement

- Gary Sang, Adrian Acosta, Kevin Fitzell, Calvin Pham, Diana Chien, Jeff Chang, Colin Rementer, Nick Altieri, Ryan Sheil, Jack Chen, Ernest Chen, Younghee Kim
- Yantao Xia, Philippe Sautet, Greg Carman, UCLA and TANMS
- J. Mark Martirez, Emily Carter, UCLA and Princeton
- Meihua Shen, Thorsten Lill, Shuogang Huang and John Hoang at Lam Research
- Intel, IBM, Samsung
- Center for Design-Enabled Nanofabrication at UC (C-DEN)
- Semiconductor Research Corporation
- National Science Foundation (TANMS ERC Center)