Plasma Chemistries for Patterning Complex Metal Oxide Materials

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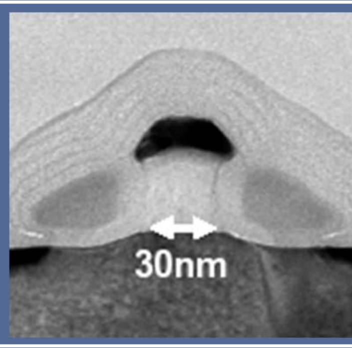
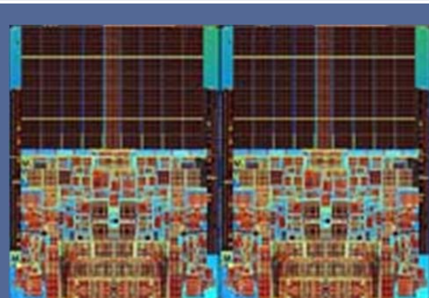
Challenges at the Atomic Scale

A Single Transistor
→Binary code
→Atomic scale
→Smaller is faster
→Reliability issue



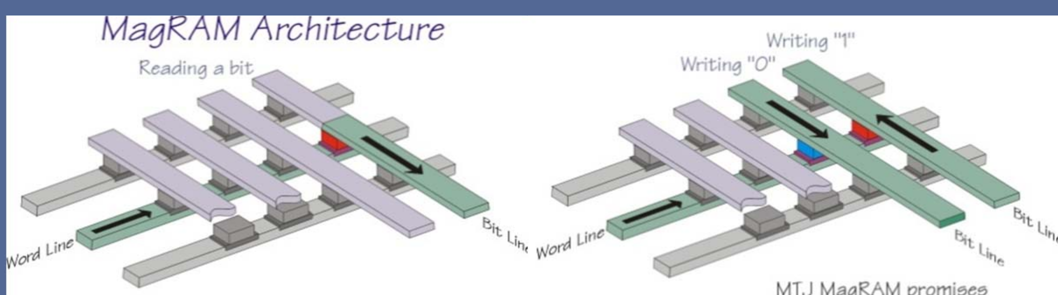
Atomic Layer Deposition
→Two site-specific self-limiting half reactions
→Atomic scale controllability
→Tailored composition and engineered interface
→Highly conformal deposition over 3-D features

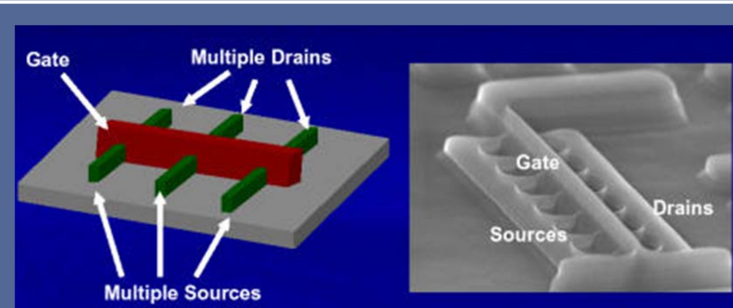
A Billion Transistors
→Integration
→Pattern fidelity
→Reaction selectivity
→Reliability issue



Intel® Core™2 Quad-core

Plasma Assisted Pattern Transfer
→Compatibility with IC manufacturing
→Highly direction ions for pattern fidelity
→Controlled ion energy, type and ratio to radicals
→Integration with wet surface chemistry

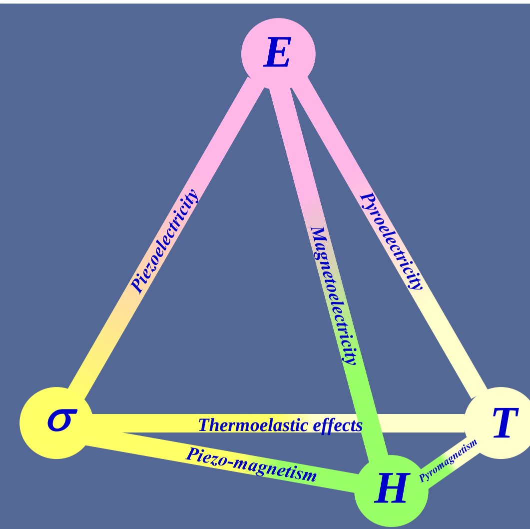


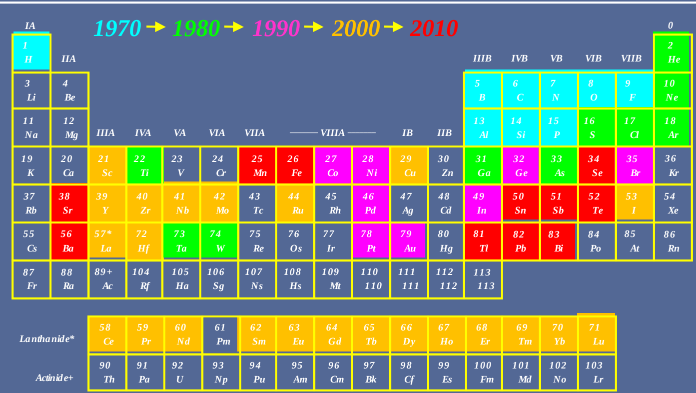


- A highly selective process is critical in enabling the device integration

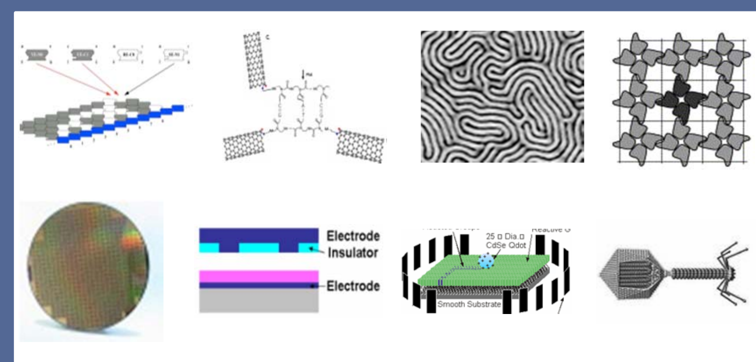
Multifunctional Oxide Materials

- Properties
  - — Insulator, semiconductor, metal
  - — Ferroelectricity; piezoelectricity; superconductivity
  - — Tunable band gap and high breakdown strength
  - — High thermal stability and low thermal conductivity
  - — Good wear, chemical, and thermal resistance
- Applications
  - — Nano-electronics (logic and memory devices)
  - — Optoelectronics/Photonics/Sensors
  - — Photovoltaics and fuel cells



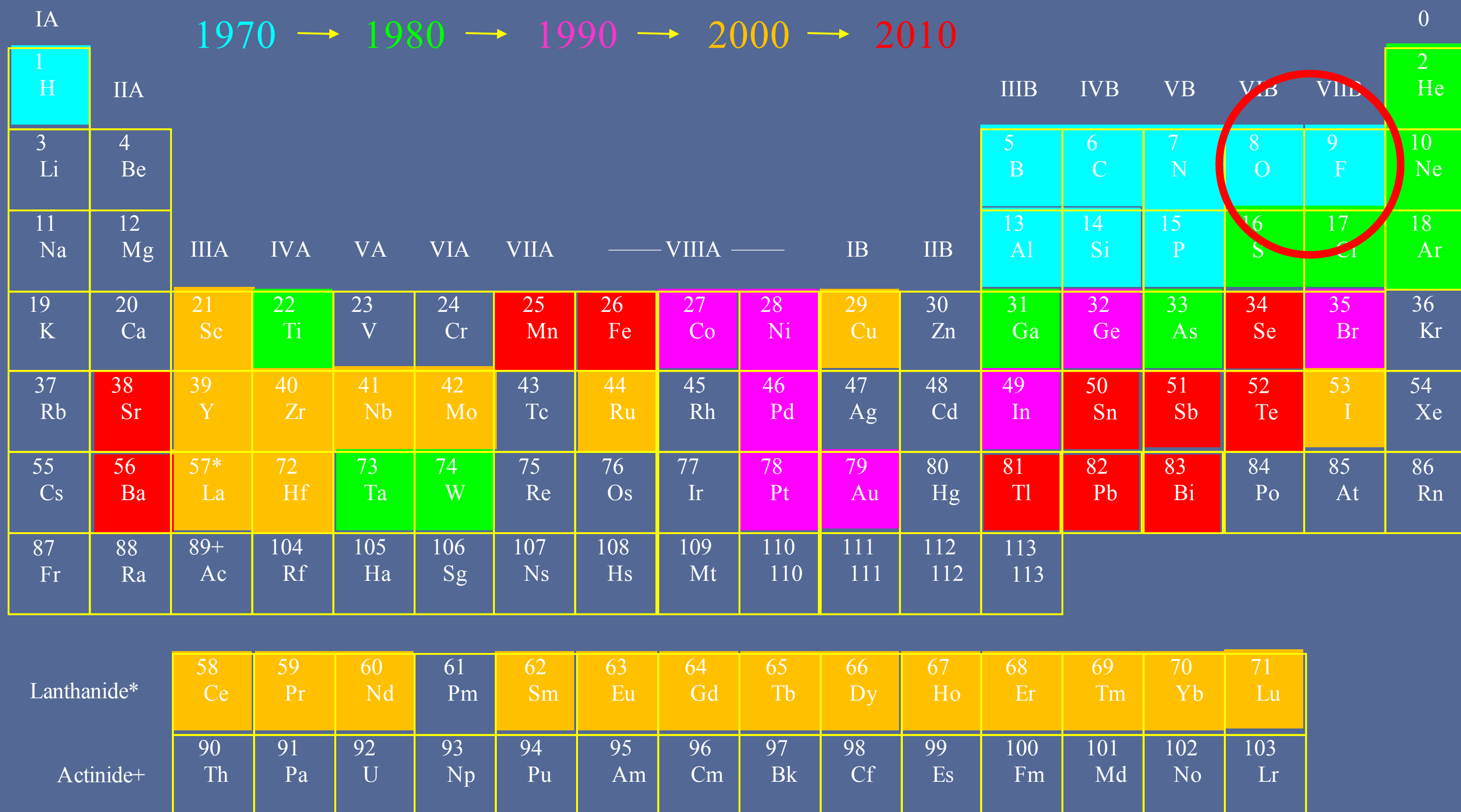


Synthesis of novel and multifunctional materials



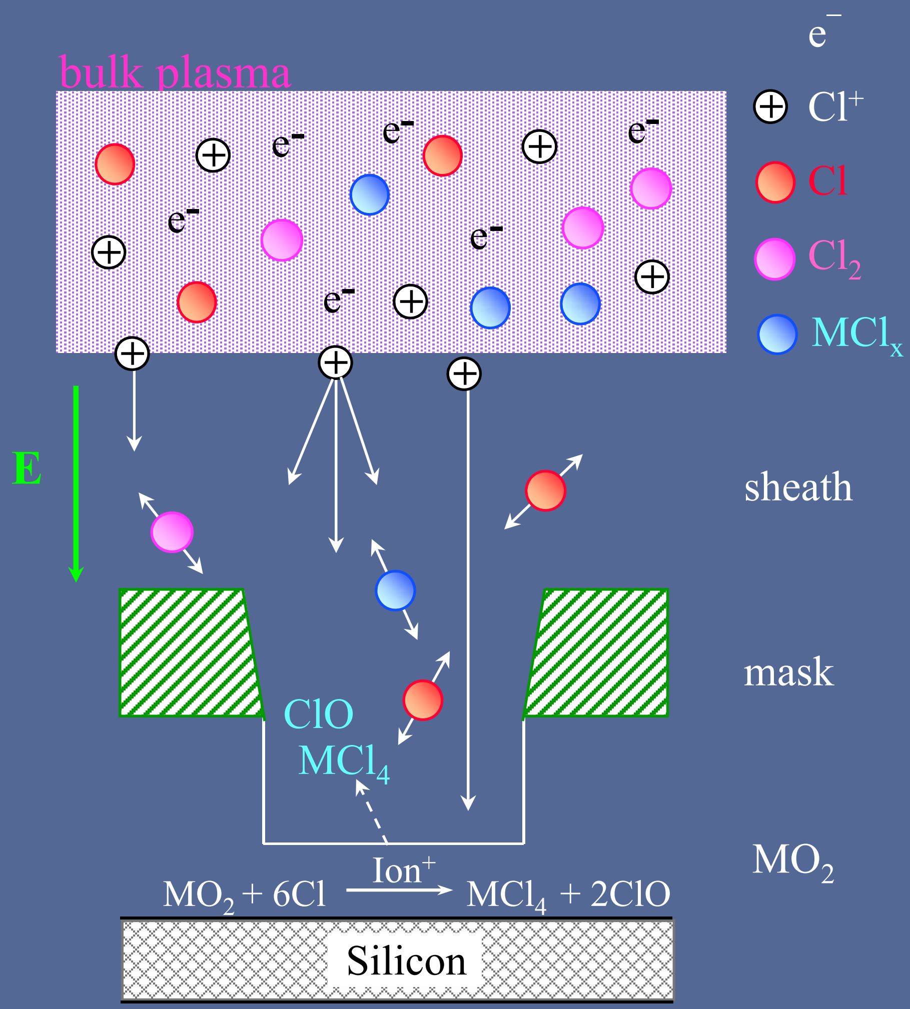
Assembly or Patterning of new materials

Challenges in Reducing PFC etchants



- Why is C_xF_y still being used? → products drive the reaction
- Issue: usage in both patterning and chamber cleaning
- How can C_xF_y be replaced? → understand the reaction

Criteria in Plasma Selection



- Etching of complex metal oxides
  - Multiple metal elements
  - Various concentrations
  - Different reactivity
- Important criteria
  - Plasma chemistry
  - Plasma density, ion energy
  - Dominant etch species
  - Metal oxygen bond strength
  - Nature of etching products
  - Heat of reaction
  - Etch product volatility

- Cl_2 and BCl_3 plasma are viable for patterning high-k dielectrics

Effect of Reaction Chemistry

Potential Reactions in Cl_2

Chemical Reactions	ΔH (kJ/mol)
$Cl_2 \xrightarrow{k_1} 2Cl$	243
$Cl + O \xrightarrow{k_2} ClO$	-268
$Al_2O_3 \xrightarrow{k_3} 2Al + 3O$	3084
$Al_2O_3 + 2Cl \xrightarrow{k_4} 2AlCl + 3O$	2085
$Al_2O_3 + 4Cl \xrightarrow{k_5} 2AlCl_2 + 3O$	1276
$Al_2O_3 + 6Cl \xrightarrow{k_6} 2AlCl_3 + 3O$	529
$Al_2O_2 + 5Cl \xrightarrow{k_7} 2AlCl + 3ClO$	1279
$Al_2O_3 + 7Cl \xrightarrow{k_8} 2AlCl_2 + 3ClO$	470
$Al_2O_3 + 9Cl \xrightarrow{k_9} 2AlCl_3 + 3ClO$	-277
$HfO_2 \xrightarrow{k_{10}} Hf + 2O$	2261
$HfO_2 + 4Cl \xrightarrow{k_{11}} HfCl_4 + 2O$	271
$HfO_2 + 6Cl \xrightarrow{k_{12}} HfCl_4 + 2ClO$	-264

Potential Reactions in BCl_3

Chemical Reactions	ΔH (kJ/mol)
$BCl_3 + \frac{1}{2}O_2 \longrightarrow \frac{1}{3}(BOCl)_3 + Cl_2$	-141
$Al_2O_3 + 3BCl_{3(g)} \longrightarrow 2AlCl_{3(g)} + (BClO)_{3(g)}$	84
$Al_2O_3 + 6BCl_{3(g)} \longrightarrow 2AlCl_{3(g)} + 3B_2OCl_{4(g)}$	286
$Al_2O_3 + \frac{9}{2}BCl_{3(g)} \longrightarrow 2AlCl_{3(g)} + \frac{3}{2}B_3O_2Cl_{5(g)}$	250
$HfO_2 + 2BCl_{3(g)} \longrightarrow HfCl_{4(g)} + \frac{2}{3}(BClO)_{3(g)}$	-58
$HfO_2 + 4BCl_{3(g)} \longrightarrow HfCl_{4(g)} + 2B_2OCl_{4(g)}$	79
$HfO_2 + 3BCl_{3(g)} \longrightarrow HfCl_{4(g)} + B_3O_2Cl_{5(g)}$	53

Species Volatility

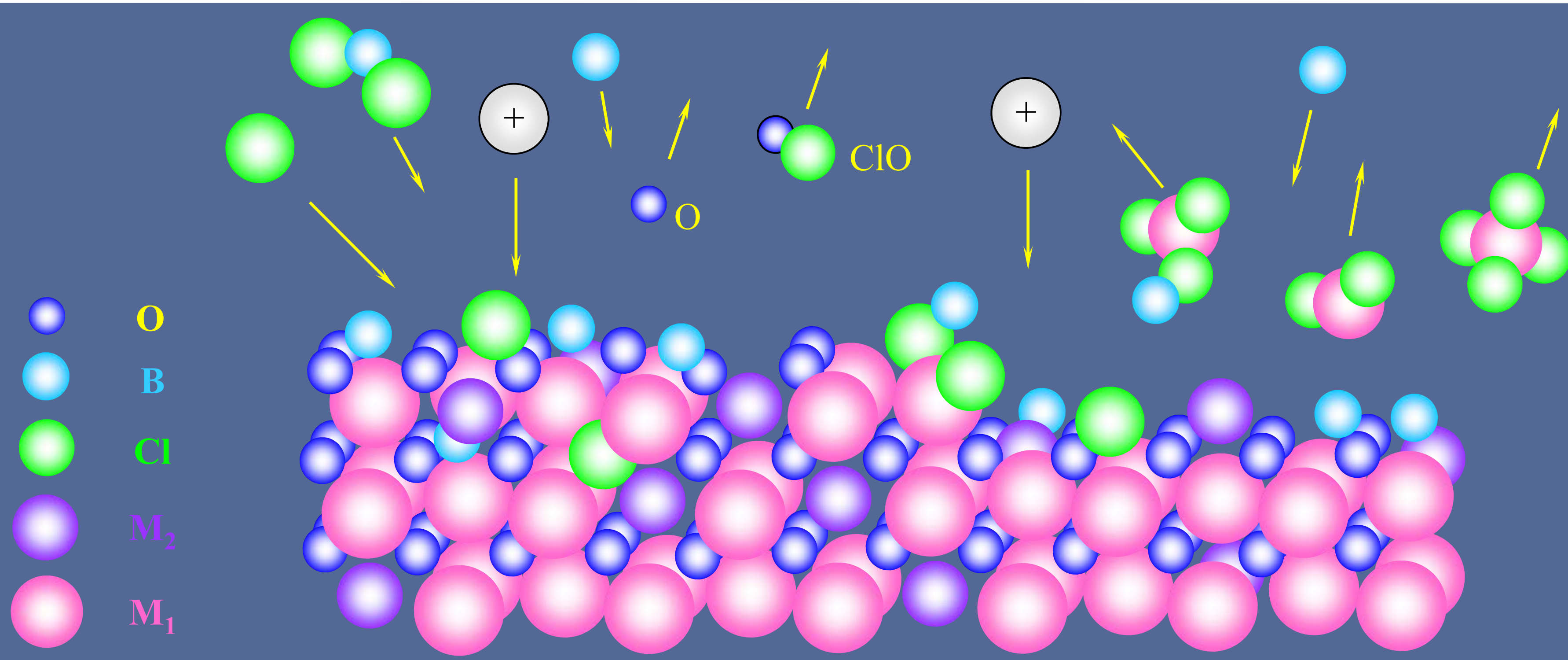
Metal Halides	Sublimation Pt. (°C)
AlF_3	1276
$AlCl_3$	180
HfF_4	970
$HfCl_4$	317

Bond Strength

Bond	Bond Strength (eV)
Al-O	5.31
Al-Cl	5.31
Hf-O	8.32
Hf-Cl	5.16

- MCl_x, ClO, and $(BOCl)_3$ formation drives the etching reactions

Etching Mechanism Analysis



- Breaking M-O bond is the critical step
    - —Chemically enhanced process → ClO, $(BOCl)_3$
- Cl radicals react with M to form volatile MCl_x
- Complexity of surface reactions (similar trends for $HfSi_xO_yN_z$)
    - —Simplifications necessary for modeling

Model Formulation

$$E_{ion} > E_{th,s} \quad \left(E_{th,s} > E_{th,p}\right)$$

Etch rate of metal oxide

$$\left(ER\right)_s = J_i A_s \left(E_{ion}^{1/2} - E_{th,s}^{1/2}\right)\theta_{es} + J_i B_s \left(E_{ion}^{1/2} - E_{tr,s}^{1/2}\right)\theta_{es}$$

$$= J_e v_{es} S_{es} \theta_1$$

Deposition rate on metal oxide

$$\left(DR\right)_s = D_s \theta_{ds} = J_d v_{ds} S_{ds} \theta_1$$

Etch rate of polymer

$$\left(ER\right)_p = J_i C_p \left(E_{ion}^{1/2} - E_{th,p}^{1/2}\right)\theta_{ep} = J_e v_{ep} S_{ep} \theta_2$$

Deposition rate of polymer

$$\left(DR\right)_p = D_p \theta_{dp} = J_d v_{dp} S_{dp} \theta_2$$

Site balance

$$\theta_s + \theta_p = 1 \Rightarrow \theta_1 + \theta_{es} + \theta_{ds} + \theta_2 + \theta_{ep} + \theta_{dp} = 1$$

Total reaction rate:

$$R_t = \left(ER\right)_s - \left(DR\right)_s + \left(ER\right)_p - \left(DR\right)_p$$

$$= \left(ER\right)_s - \left(DR\right)_p$$

$$= J_i A_s \left(E_{ion}^{1/2} - E_{th,s}^{1/2}\right)\theta_{es} + J_i B_s \left(E_{oni}^{1/2} - E_{tr,s}^{1/2}\right)\theta_{es} - D_p \theta_{dp}$$

Summary of Rate Model Parameters

Parameter	Definition	Units
J_i	Positive ion flux	$\#/\text{Å}^2 s$
J_e	Etching Species flux	
J_d	Depositing species flux	
E_{ion}	Positive ion energy	eV
$E_{th,s}$	Substrate etching threshold energy	
$E_{tr,s}$	Substrate etching transition energy	
$E_{th,p}$	Polymerching threshold energy	
v_{es}	Volume of substrate removed per etching species	$\text{Å}^3/\#$
v_{ds}	Volume of polymer grown on substrate per depositing species	
v_{ep}	Volume of polymer removed per etching species	
v_{dp}	Volume of polymer grown on polymer per depositing species	
S_{es}	Reactive sticking probability of etching species on substrate	*unitless*
S_{ds}	Reactive sticking probability of depositing species on substrate	
S_{ep}	Reactive sticking probability of etching species on polymer	
S_{dp}	Reactive sticking probability of depositing species on polymer	
A_s	Volume of substrate removed per unit bombardment energy due to ion mixing-induced desorption	$\text{Å}^3/eV^{1/2}$
B_s	Volume of substrate removed per unit bombardment energy due to ion-enhanced chemical etching	
C_p	Volume of polymer removed per unit bombardment energy due to ion-enhanced chemical etching	
D_s	Depositiong rate of polymer on substrate	$\text{Å}/s$
D_p	Depositiong rate of polymer on polymer	

$$Z_{\alpha\gamma} = v_{\alpha\gamma} S_{\alpha\gamma}$$

Model Development

$$R_t = \frac{J_e^2 v_{es} S_{es} v_{ep} S_{ep} - J_d^2 v_{ds} S_{ds} v_{dp} S_{dp}}{J_e v_{ep} S_{ep} + \frac{J_d^2 v_{ds} S_{ds} v_{dp} S_{dp}}{D_p} + \frac{J_d J_e v_{ds} S_{ds} v_{ep} S_{ep}}{J_i C_p \left(E_{ion}^{1/2} - E_{th,p}^{1/2}\right)} + J_d v_{ds} S_{ds} + \frac{J_d J_e v_{ds} S_{ds} v_{ep} S_{ep}}{D_s} + \frac{J_e^2 v_{es} S_{es} v_{ep} S_{ep}}{J_i \left[A_s \left(E_{ion}^{1/2} - E_{th,s}^{1/2}\right) + B_s \left(E_{ion}^{1/2} - E_{tr,s}^{1/2}\right)\right]}}$$

$J_d = 0$

$$R_t = \frac{J_i \left[A_s \left(E_{ion}^{1/2} - E_{th,s}^{1/2}\right) + B_s \left(E_{ion}^{1/2} - E_{tr,s}^{1/2}\right)\right]}{1 + J_i \left[A_s \left(E_{ion}^{1/2} - E_{th,s}^{1/2}\right) + B_s \left(E_{ion}^{1/2} - E_{tr,s}^{1/2}\right)\right] \Big/ J_e v_{es} S_{es}}$$

$J_e = 0$

$$R_t = -\frac{J_d v_{dp} S_{dp}}{1 + J_d v_{dp} S_{dp} / D_p}$$

$E_{th,p} < E_{ion} < E_{th,s}$

$$R_t = (E.R.)_{ep} - (D.R.)_{dp} = J_i C_p \left(E_{ion}^{1/2} - E_{th,p}^{1/2}\right) - J_d Z_{dp}$$

$E_{ion} < E_{th,p}$

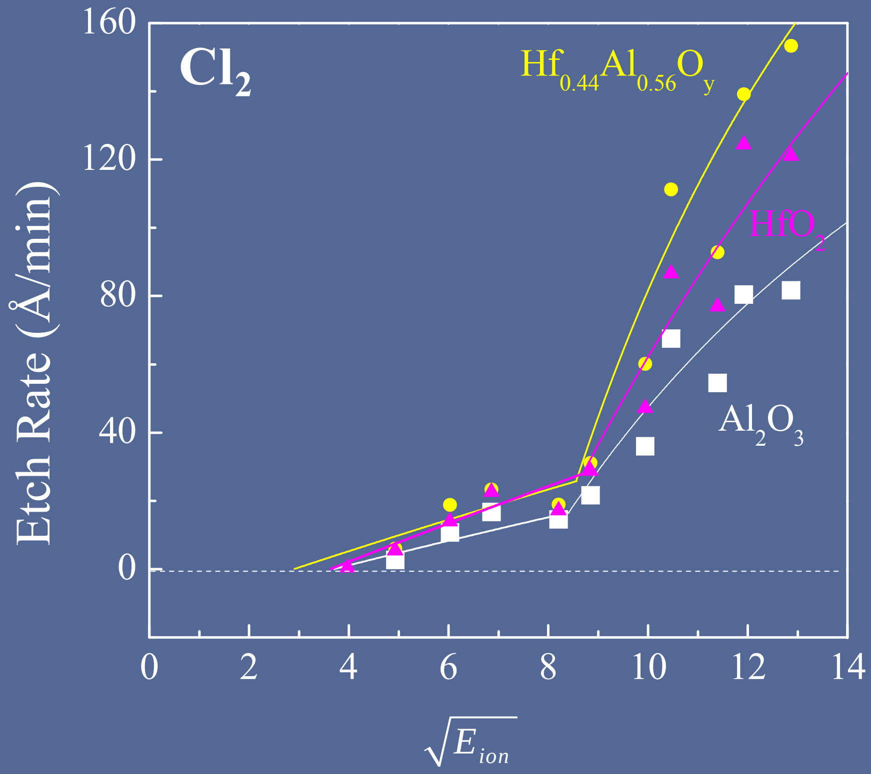
$$R_t = -(D.R.)_{dp} = -J_d v_{dp} S_{dp} = -J_d Z_{dp}$$

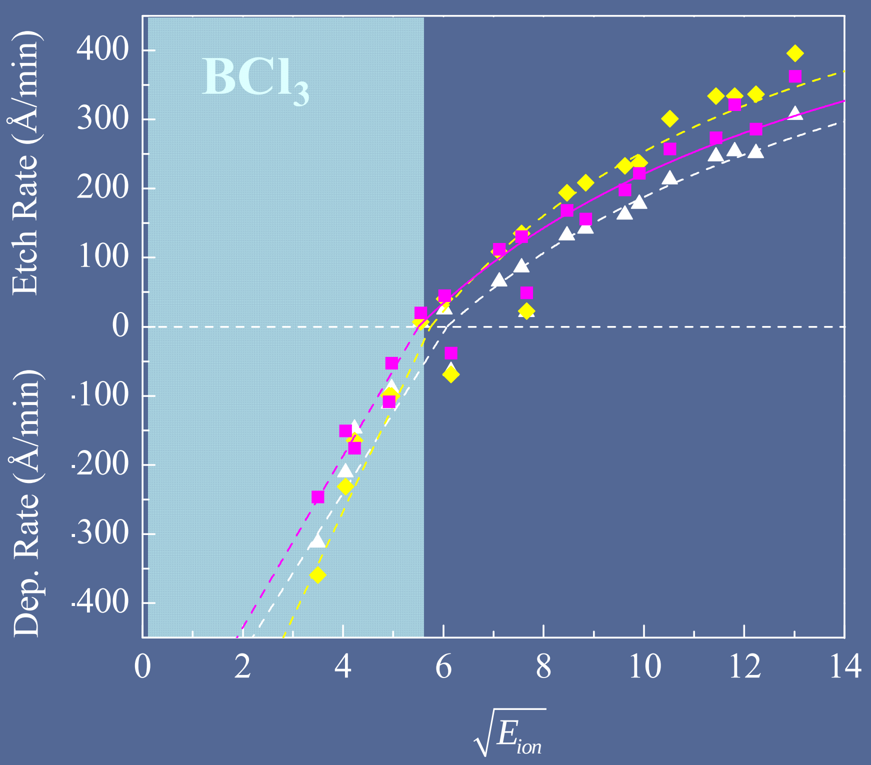
$-(D.R.)_{dp}$ = 300 Å/min
J_d = 26 #/Å^{2}s
S_{dp} of BCl_x ranges 0.001 to 0.1*
→ v_{dp} ~ 19 Å^3

* Choi and Veerasingam JVST A **16**(3), 1873 (1998).

Plasma Etch Modeling

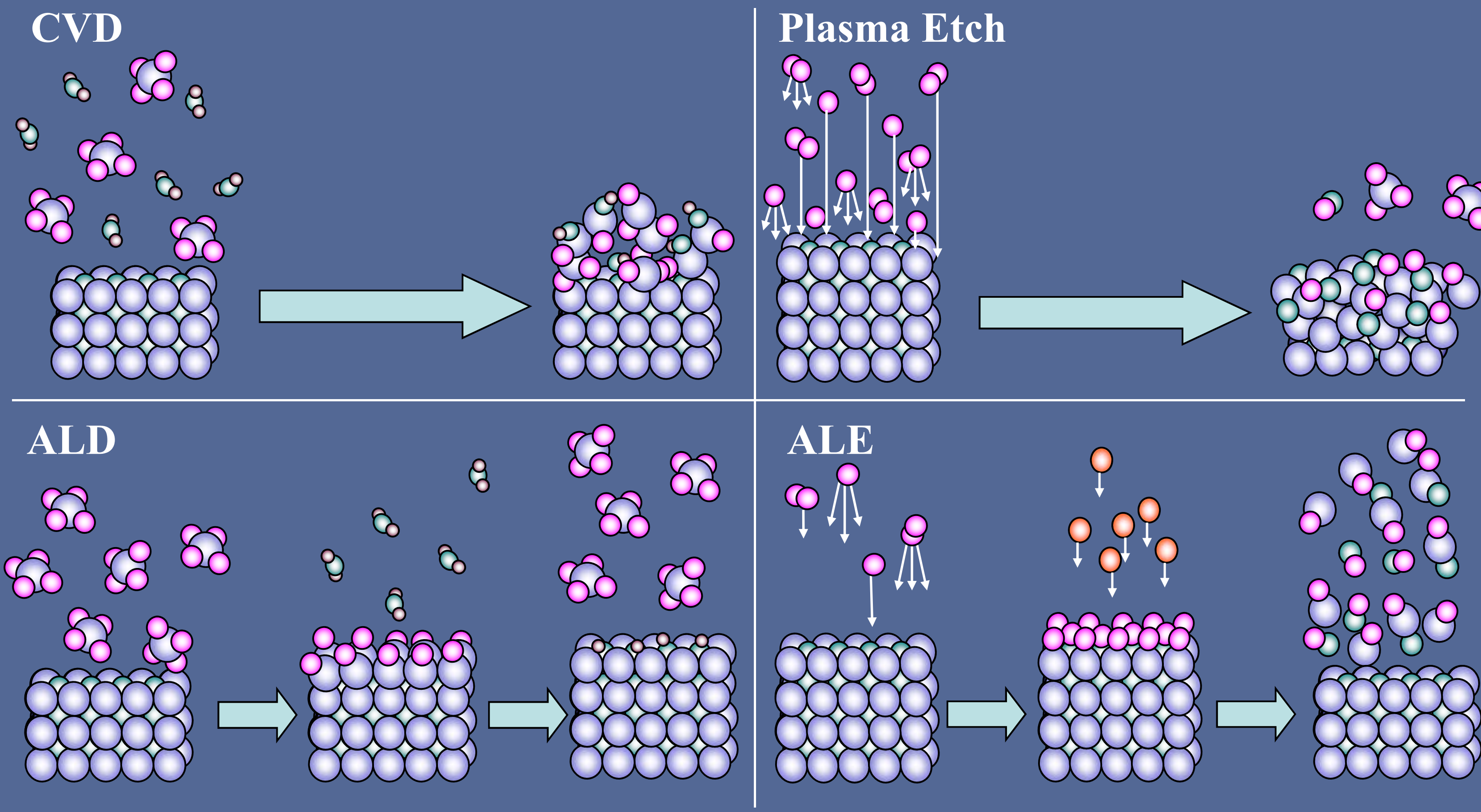
$$R_t = \frac{J_e^2 v_{es} S_{es} v_{ep} S_{ep} - J_d^2 v_{ds} S_{ds} v_{dp} S_{dp}}{J_e v_{ep} S_{ep} + \frac{J_d^2 v_{ds} S_{ds} v_{dp} S_{dp}}{D_p} + \frac{J_d J_e v_{ds} S_{ds} v_{ep} S_{ep}}{J_i C_p \left(E_{ion}^{1/2} - E_{th,p}^{1/2}\right)} + J_d v_{ds} S_{ds} + \frac{J_d J_e v_{ds} S_{ds} v_{ep} S_{ep}}{D_s} + \frac{J_e^2 v_{es} S_{es} v_{ep} S_{ep}}{J_i \left[A_s \left(E_{ion}^{1/2} - E_{th,s}^{1/2}\right) + B_s \left(E_{ion}^{1/2} - E_{tr,s}^{1/2}\right)\right]}}$$





- The model addresses flux/energy dependence and etch/deposition competition

ALD vs. 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 MO_2:

(1) $MO_2(s)+Cl^+(g) \rightarrow MO_2^*(s)$

(2) $MO_2^*(s)+ 6Cl(g) \rightarrow MCl_4(g)+2OCl(g)$

Challenges and Opportunities

Challenges: PFC replacement would have to meet all patterning criteria (etch rate, profile control, selectivity) provide a smaller GWP footprint.

Opportunities: Investigate targeting gases and applications where the processing risk vs. GWP reward is large.

Plasma processing capabilities, analytical tools and modeling capabilities will be required for successful completion of this task.

Proposed Milestones (timing TBD):
- Identify high impact gases and plasma etch applications
- Develop, analyze and test performance of alternative gases.
- Develop and utilize modeling to predict PFC replacement strategies