Deposition and Patterning of Zirconium and Hafnium Oxide as High-k Gate Dielectrics

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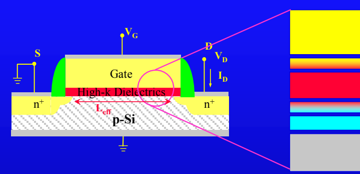
Scaling of the Gate Dielectrics

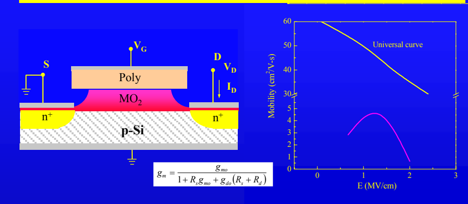


$$I_D^{sat} = \frac{W}{L_{eff}} \mu C_{inv} \frac{(V_G - V_T)^2}{2}$$

$$C = \frac{\kappa \varepsilon_0 A}{t}$$

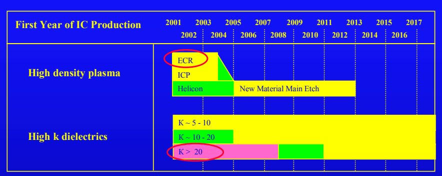
High-k material is needed !!
(Or an alternative transistor design)
But, what else is going on ??

Integration Challenges



- Low transconductance: 3.5×10^{-5} S
- Interfacial layer causes source and drain resistances: 2 A of $ZrSiO_4$ (Resistivity of zirconium oxide is 1×10^{12} μΩ-cm)
- Plasma etching is needed to pattern high-k materials

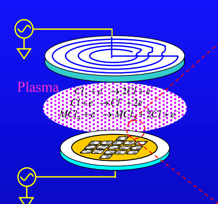
Roadmap for Etching



International Technology Roadmap for Semiconductors (2001)

- Reasons and challenges for high-κ dielectric materials:
  — Etchable

Plasma Etching of ZrO_2 and HfO_2

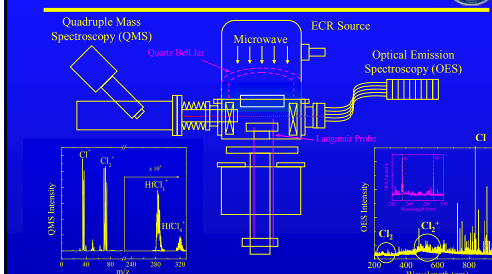


Surface reactions lead to directional profile and low substrate damage

	Sublimation point (°C)
$ZrCl_4$	331
$HfCl_4$	317

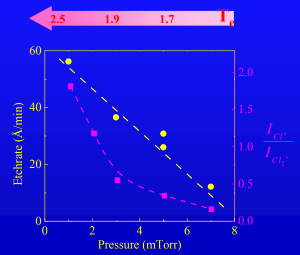
Chemical Reaction	ΔH (kJ/mol)		
		M = Zr	M = Hf
$Cl_2 \xrightarrow{k_1} 2Cl$	243		
$Cl + O \xrightarrow{k_2} ClO$	-268		
$MO_2 \xrightarrow{k_3} M + 2O$		2208	2261
$MO_2 + Cl \xrightarrow{k_4} MCl + 2O$			
$MO_2 + 2Cl \xrightarrow{k_5} MCl_2 + 2O$		854	
$MO_2 + 3Cl \xrightarrow{k_6} MCl_3 + 2O$			
$MO_2 + 4Cl \xrightarrow{k_7} MCl_4 + 2O$		133	273
$MO_2 + 3Cl \xrightarrow{k_8} MCl + 2ClO$			
$MO_2 + 4Cl \xrightarrow{k_9} MCl_2 + 2ClO$		317	
$MO_2 + 5Cl \xrightarrow{k_{10}} MCl_3 + 2ClO$			
$MO_2 + 6Cl \xrightarrow{k_{11}} MCl_4 + 2ClO$		-404	-264

Plasma Diagnostics



- Quantify chemical species in the plasma through OES and QMS

Effect of T_e



- Power = 500 W
- E_{ion} ~ 82 eV

$Cl_2 + e^- \rightarrow Cl + Cl + e^-$

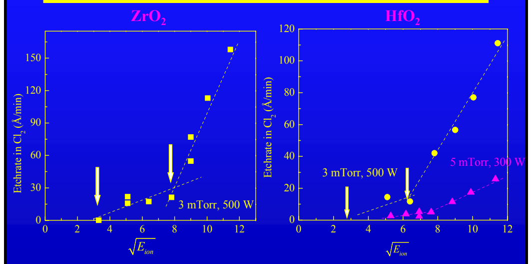
$Cl_2 + e^- \rightarrow Cl_2^+ + 2e^-$

$Cl_2 + e^- \rightarrow Cl^+ + Cl + 2e^-$

$Cl + e^- \rightarrow Cl^+ + 2e^-$

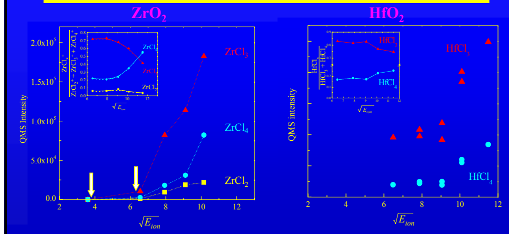
- Etching rate decreases with increased chamber pressure

Effect of Ion Energy (in Cl_2)



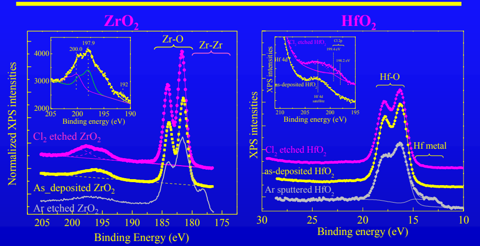
- ZrO_2 and HfO_2 etching rate increases with increased ion energy

Etching Products in Cl_2



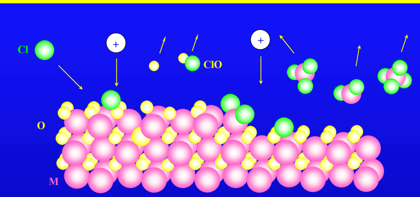
- 3 mTorr and 500 W, surface chlorination confirmed by XPS
- $ZrCl_3$ and $HfCl_3$ are the primary etching products at low ion energies
- ZrO_2 and HfO_2 etch products are different

Surface Composition (Cl_2)



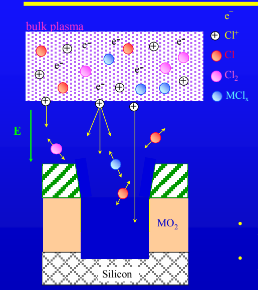
- Chlorine was found on plasma etched surface

Etching Mechanism Analysis



- Breaking M-O bond is the critical step
  - — Physical sputtering → O
  - — Chemical etching → ClO
- Cl radicals react with M to form volatile MCl_x

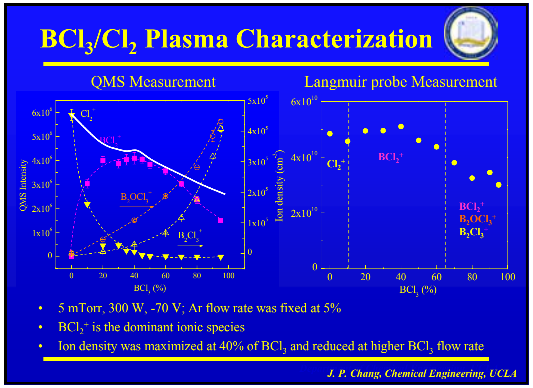
Etching Selectivity to Si



	Bond strength (eV)
Hf-O	8.32
Hf-Cl	5.16
Zr-O	8.06
Zr-Cl	5.11
Si-O	8.30
Si-Cl	4.22
Si-Si	3.39
Si-B	2.99
B-O	8.40
B-Cl	5.31

$$ZrO_2 + 2BCl_3 \rightarrow ZrCl_4 + 2BClO$$
$$Si + B \rightarrow BSi$$
$$HfO_2 + 2BCl_3 \rightarrow HfCl_4 + 2BClO$$

- Boron could enhance the oxygen removal by forming volatile species
- Boron would passivate the silicon surface by forming B-Si bonds


BCl3/Cl2 Plasma Characterization
QMS Measurement
Langmuir probe Measurement
QMS Intensity
Ion density (cm-3)
BCl3 (%)
BCl2+
B2OCl3+
B2Cl3+
• 5 mTorr, 300 W, -70 V; Ar flow rate was fixed at 5%
• BCl2+ is the dominant ionic species
• Ion density was maximized at 40% of BCl3 and reduced at higher BCl3 flow rate
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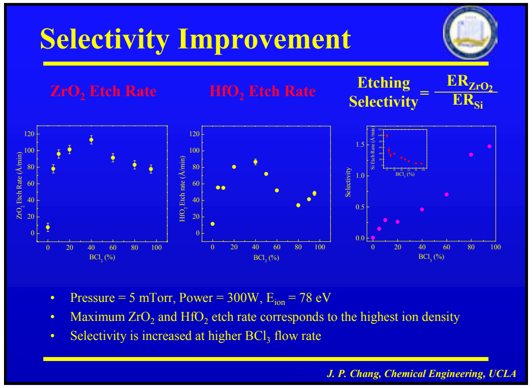
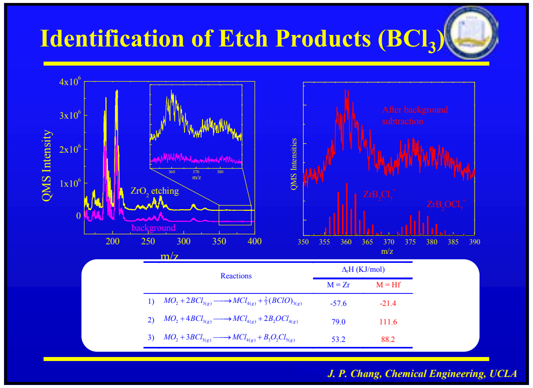

Selectivity Improvement
ZrO2 Etch Rate
HfO2 Etch Rate
Etching Selectivity = ERZrO2 / ERSi
BCl3 (%)
• Pressure = 5 mTorr, Power = 300W, Eion = 78 eV
• Maximum ZrO2 and HfO2 etch rate corresponds to the highest ion density
• Selectivity is increased at higher BCl3 flow rate
J. P. Chang, Chemical Engineering, UCLA


Identification of Etch Products (BCl3)
QMS Intensity
ZrO2 etching
background
m/z
After background subtraction
Reactions
ΔH (KJ/mol)
M = Zr
M = Hf
-57.6
-21.4
79.0
111.6
53.2
88.2
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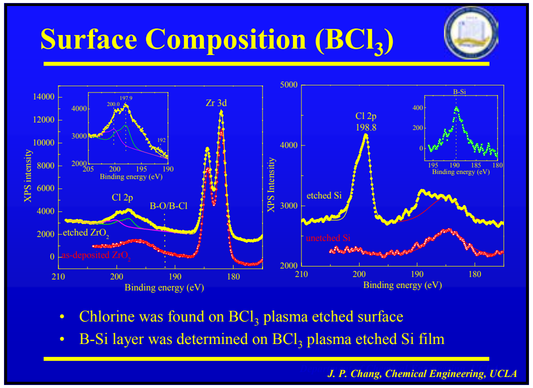
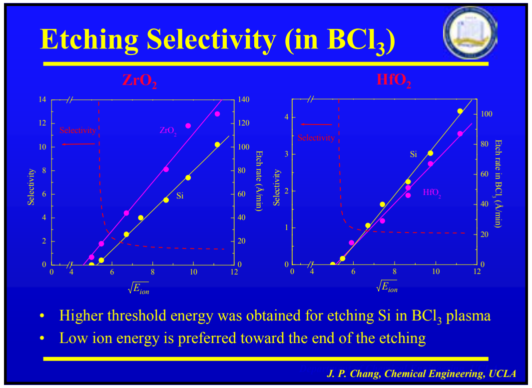

Surface Composition (BCl3)
XPS intensity
Binding energy (eV)
Zr 3d
Cl 2p
B-O/B-Cl
etched ZrO2
as-deposited ZrO2
Cl 2p 198.8
B-Si
etched Si
unetched Si
• Chlorine was found on BCl3 plasma etched surface
• B-Si layer was determined on BCl3 plasma etched Si film
J. P. Chang, Chemical Engineering, UCLA


Etching Selectivity (in BCl3)
ZrO2
HfO2
Selectivity
Etch rate (Å/min)
Si
• Higher threshold energy was obtained for etching Si in BCl3 plasma
• Low ion energy is preferred toward the end of the etching
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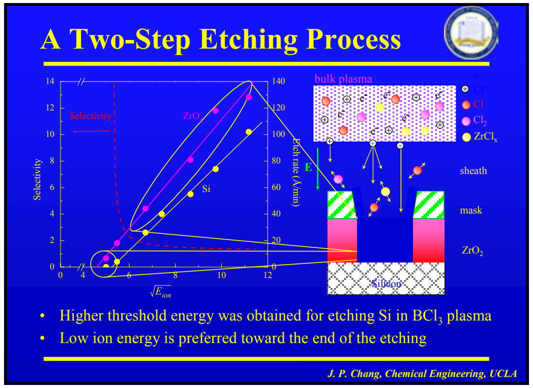
A Two-Step Etching Process
Selectivity
ZrO2
Si
bulk plasma
Cl
Cl2
ZrClx
sheath
mask
ZrO2
Silicon
• Higher threshold energy was obtained for etching Si in BCl3 plasma
• Low ion energy is preferred toward the end of the etching
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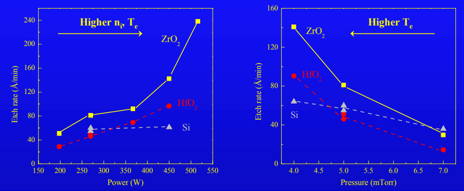
Effect of T_e on Etching Selectivity

BCl_3 Plasma, E_{ion} ~ 75 eV



- ZrO_2 and HfO_2 have similar responses to T_e and n_i
- Si is less sensitive to the plasma variations
- High power and low pressure is preferred for higher selectivity

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Formulation of Reaction Model

$$ER_{MO_2} = \alpha \cdot n_i^{\beta} \cdot n_{Cl}^{\gamma} \cdot E_{M\text{-}O}^{\delta} \cdot \left(\sqrt{E_{ion}} - \sqrt{\varepsilon \cdot E_{M\text{-}O}^{\Theta}}\right)$$

ER_{MO2}: etch rate of MO_2 in BCl_3 (Å/min)
n_i: ion density (QMS BCl_2^+)
n_{Cl}: neutral density (OES I_{Cl}/I_{Ar})
E_{ion}: ion energy (eV)
$E_{M\text{-}O}$: bond strength (eV)

Parameters	Fitting values
α	1.56×10^9
β (n_i)	0.63
γ (n_{Cl})	1.11
δ ($E_{M\text{-}O}$)	- 11.5
ε (E_{th})	1.78×10^{-5}
θ ($E_{M\text{-}O}$)	6.71

$$E_{th} = \varepsilon \cdot E_{M-O}^{\theta} \Rightarrow \varepsilon \text{ and } \theta$$

$$\frac{ER_{ZrO_2}}{ER_{HfO_2}} = \left(\frac{E_{Zr-O}}{E_{Hf-O}}\right)^{\delta} \cdot \frac{\left(E_{ion}^{1/2} - \left(\varepsilon \cdot E_{Zr-O}^{\theta}\right)^{1/2}\right)}{\left(E_{ion}^{1/2} - \left(\varepsilon \cdot E_{Hf-O}^{\theta}\right)^{1/2}\right)} \Rightarrow \delta$$

$$\frac{ER_{MO_2}}{E_{M-O}^{\delta} \cdot \left(E_{ion}^{1/2} - \left(\varepsilon \cdot E_{M-O}^{\theta}\right)^{1/2}\right)} = \alpha \cdot n_i^{\beta} \cdot n_{Cl}^{\gamma} \Rightarrow \alpha, \beta, \text{ and } \gamma$$

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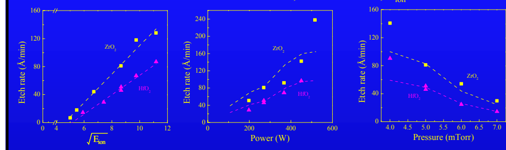
Validation with Experiments (BCl_3)

Baseline conditions: Pressure = 5 mTorr, Power = 300W, E_{ion} = 78 eV



- Model predicts well the experimental results, with some deviation at high power and low pressure (high T_e), probably due to the inaccurate Cl density measurement and neutral temperature change

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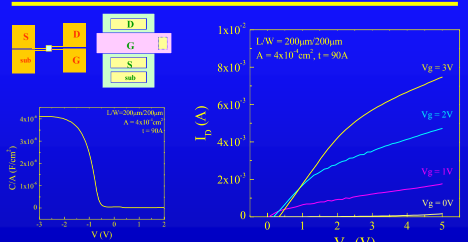
NMOSFET Device



- Plasma etching of HfO_2
- Electron mobility is ~ 200 cm^2/V-s (much higher mobility compared to NMOSFET made with ZrO_2 + HF etch)

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Conclusion

- HfO_2 is chemically etched in Cl_2 and BCl_3 plasmas and the etch rate scales with $\sqrt{E_{ion}}$
- $HfCl_3$ and $HfCl_4$ are the major etching products, and $HfCl_4$ becomes the dominant product at higher ion energy
- Surface chlorination was confirmed by XPS
- Addition of BCl_3 significantly improved the etch rate and etching selectivity
- For more complex oxides such as silicates and aluminates, plasma etching will also be required.

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