Structure-Property Relations in ALD-Grown HfO_2 Gate Dielectrics: Effects of Precursor Chemistry

R. Sreenivasan[1], P.C. McIntyre[1], K.C. Saraswat[2]

[1] Department of Materials Science Eng., Stanford University
[2] Department of Electrical Eng., Stanford University

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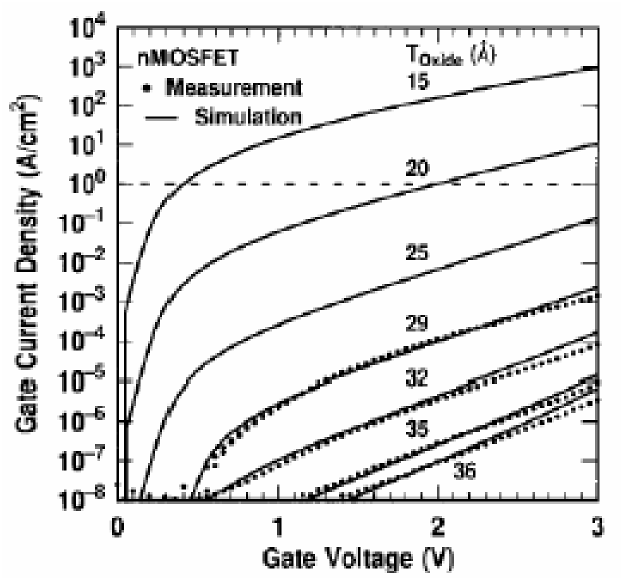
Outline

- Need for high-k dielectrics
- Atomic Layer Deposition
- Choice of Precursors
- Electrical Characteristics of HfO_2 films
- Si Surface Passivation prior to ALD
- Summary and Future Work

High-k Dielectrics

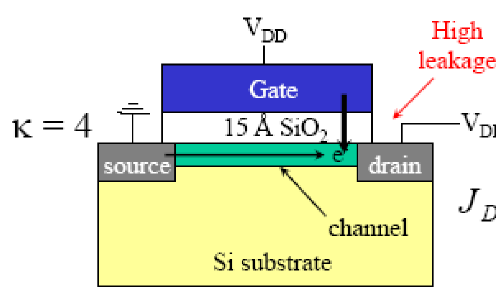


S.-H. Lo et al., IEEE Electron Device Lett. 18, 209 (1997).

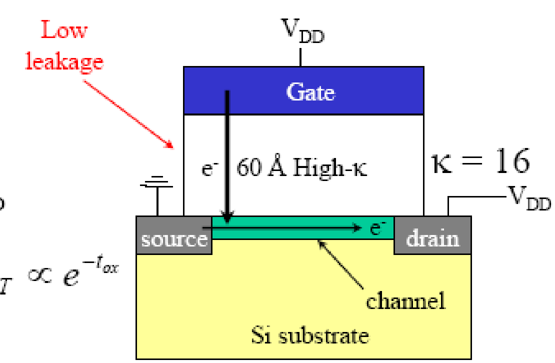
Gate leakage current increases exponentially with decrease in t_{ox}

$$C_{ox} = \frac{\kappa \varepsilon_0 A}{t_{ox}}$$

$$t_{high-\kappa} = \left(\frac{\kappa_{high-\kappa}}{\kappa_{SiO_2}} \right) \cdot t_{SiO_2}$$



$$J_{DT} \propto e^{-t_{ox}}$$



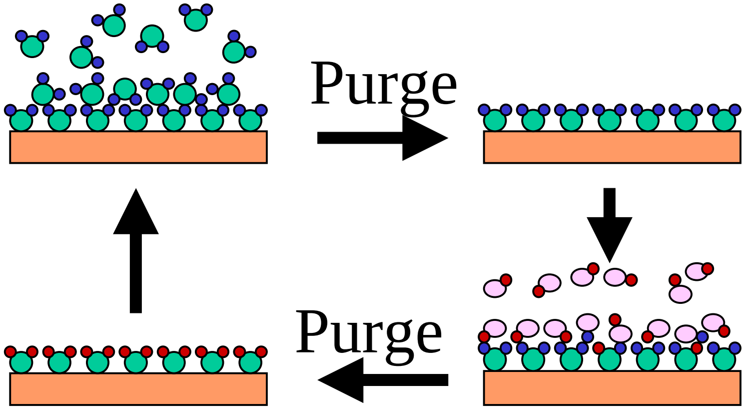
High-k Candidates

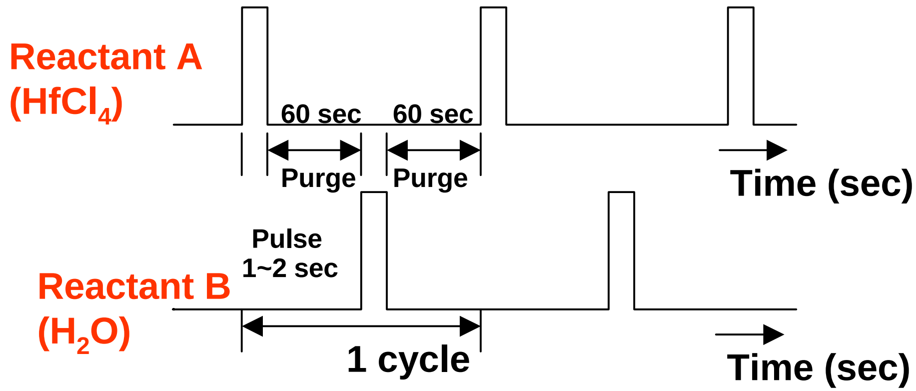
Dielectric	κ	Bandgap (eV)	ΔE_c to Si	ΔE_v to Si
SiO_2	3.9	9	3.5	4.4
Si_3N_4	7	5.3	2.4	1.8
Al_2O_3	9	8.8	2.8	4.9
ZrO_2	25	5.8	1.4	3.3
HfO_2	25	6.0	1.5	3.4

ZrO_2 and HfO_2

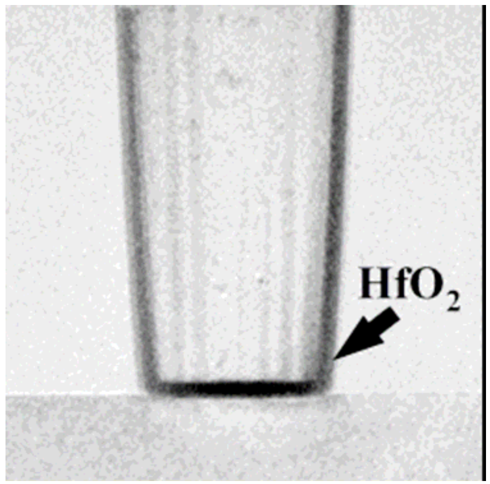
- Thermodynamically stable on Si
- Acceptable band offsets to Si
- High dielectric constant

Atomic Layer Deposition





Schematic of the ALD process



(courtesy Hyoungsub Kim)

- Self-limiting growth
- Highly conformal, low defect thin films
- Very good step coverage
- Low temperature deposition
- Excellent control over film thickness
- Uniform thickness over large areas
- Good control of stoichiometry
- Abrupt interface to the substrate

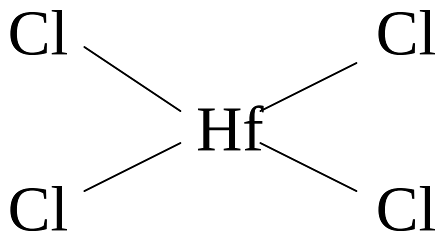
Choice of Precursors

<u>Chlorides</u>

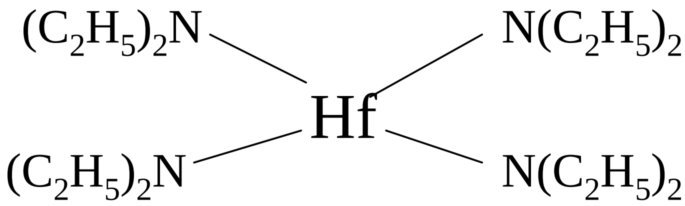
1. HCl is a by-prod of the reaction and is very corrosive
2. Chlorine contamination of the films
3. Solid source: gas line clogging and particle contamination

<u>Alkylamides</u>

1. No harmful by-products
2. No chlorine contamination
3. Liquid or low melting solid at RT
4. High growth rates

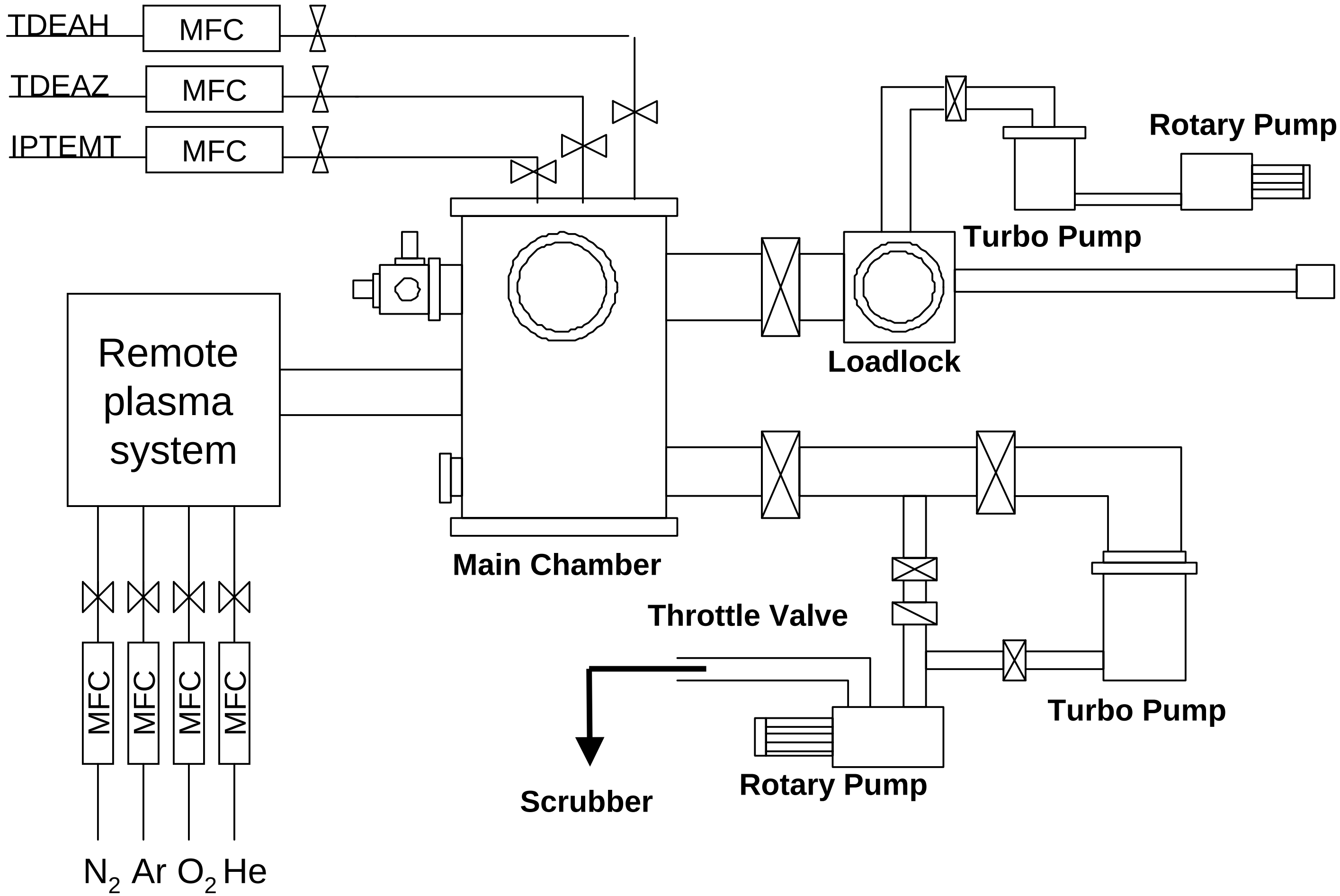


$HfCl_4$



Tetrakis(diethylamino)Hafnium
TDEAH

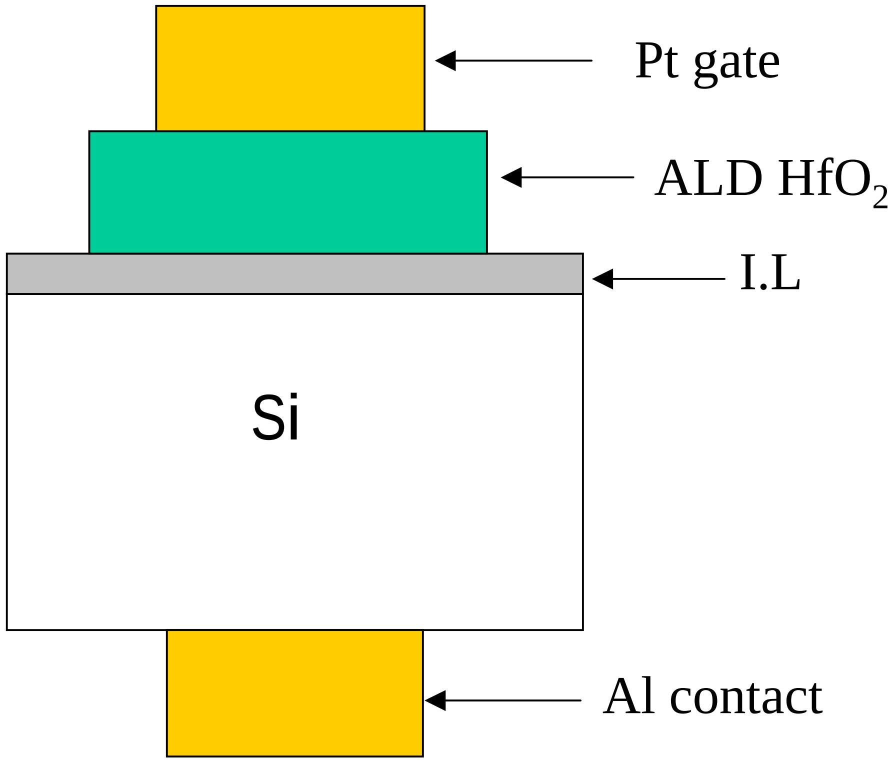
Stanford ALD Chamber



ALD Process Parameters

	$HfCl_4$	TDEAH
Substrate temp	300 °C	150 °C
Bubbler temp	150 °C	65 °C
Pulsing	1-60-1-60	1-50-1-50
Dep rate	0.5Å/cycle	0.75Å/cycle
Chamber wall	R.T	75 °C
Oxidizer	H_2O	H_2O
N_2(carrier gas)	20 sccm	2.5 sccm
Process Pr	0.5 Torr	0.5 Torr

Capacitor Structure

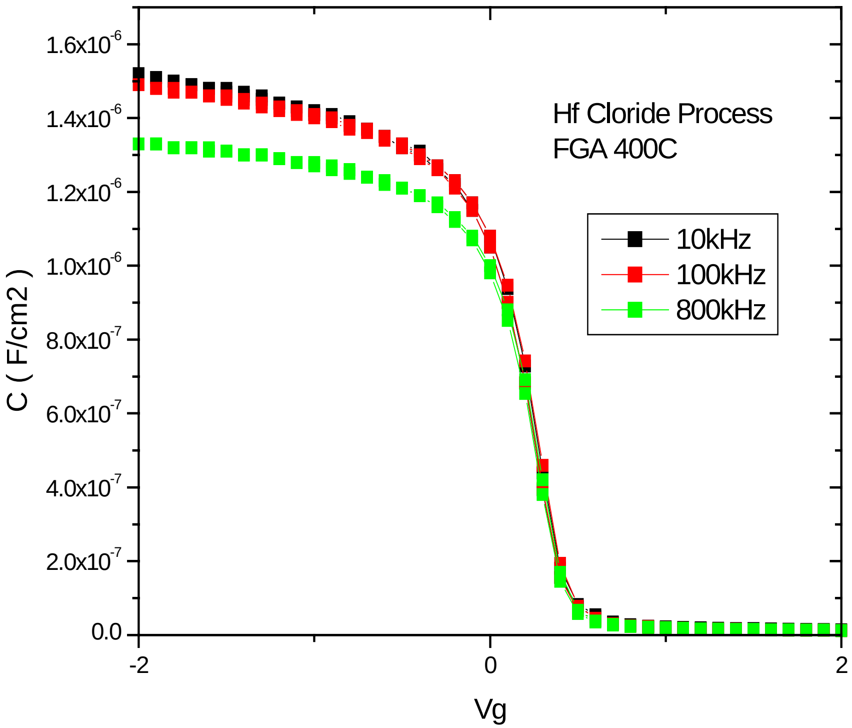


- Metal electrodes deposited by e-beam evaporation

- FGA performed at 400°C to reduce D_{it}

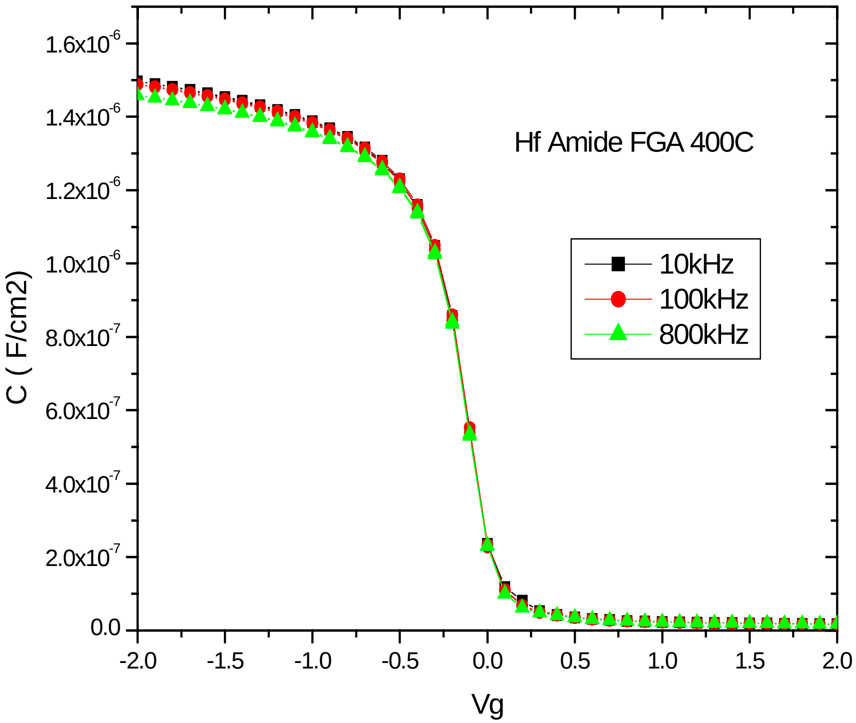
C-V Hysteresis

Chloride



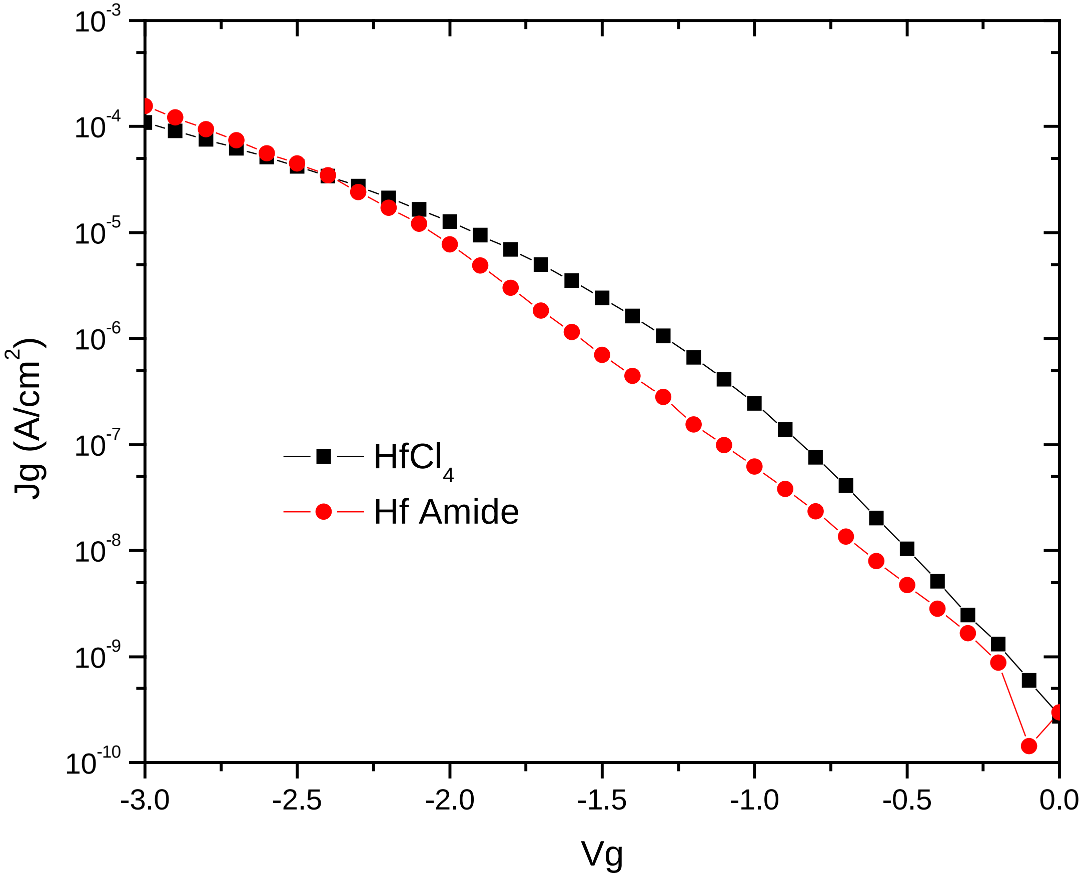
t_{HfO2} = 45Å, I.L = 15Å
Cap derived EOT = 23.1Å
Hysteresis ~ 20 mV

Alkylamide



t_{HfO2} = 50Å, I.L = 15Å
Cap derived EOT = 23.2Å
Hysteresis ~ 5 mV

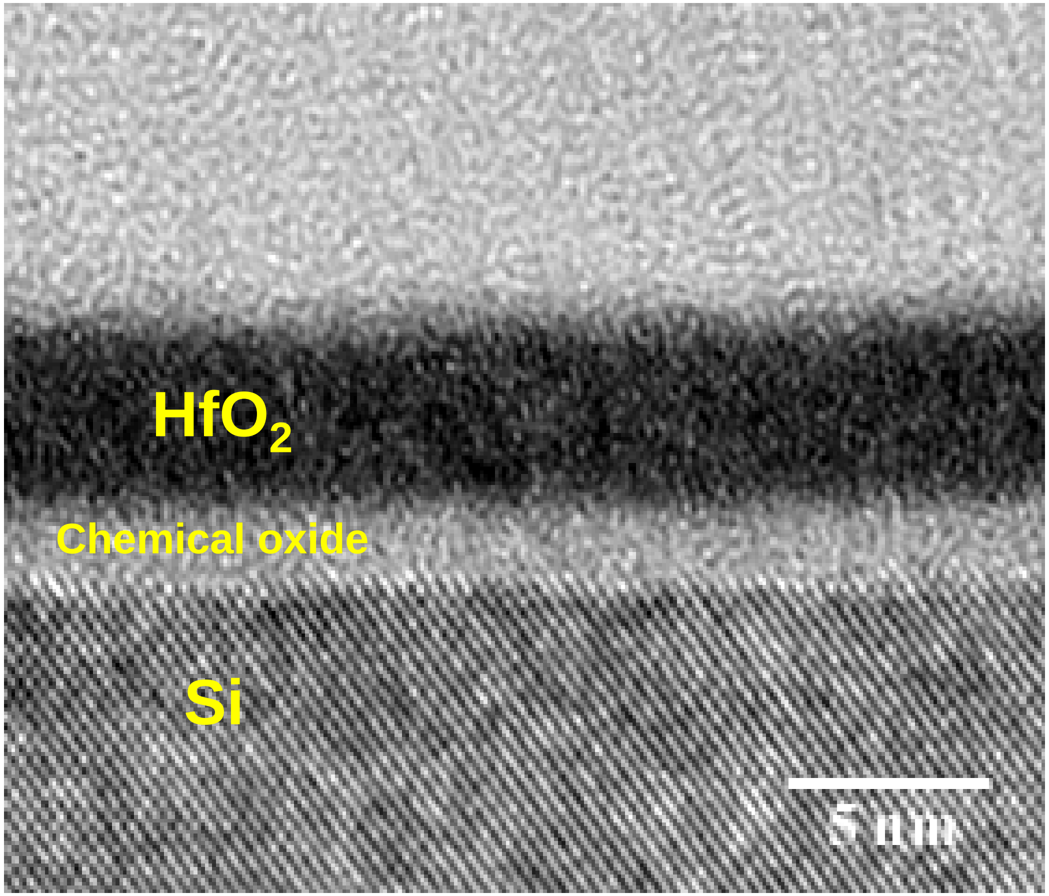
Leakage Current



Comparable leakage currents were observed on MOSCAP structures on HfO_2 grown using $HfCl_4$ and TDEAH.

EOT = 23Å

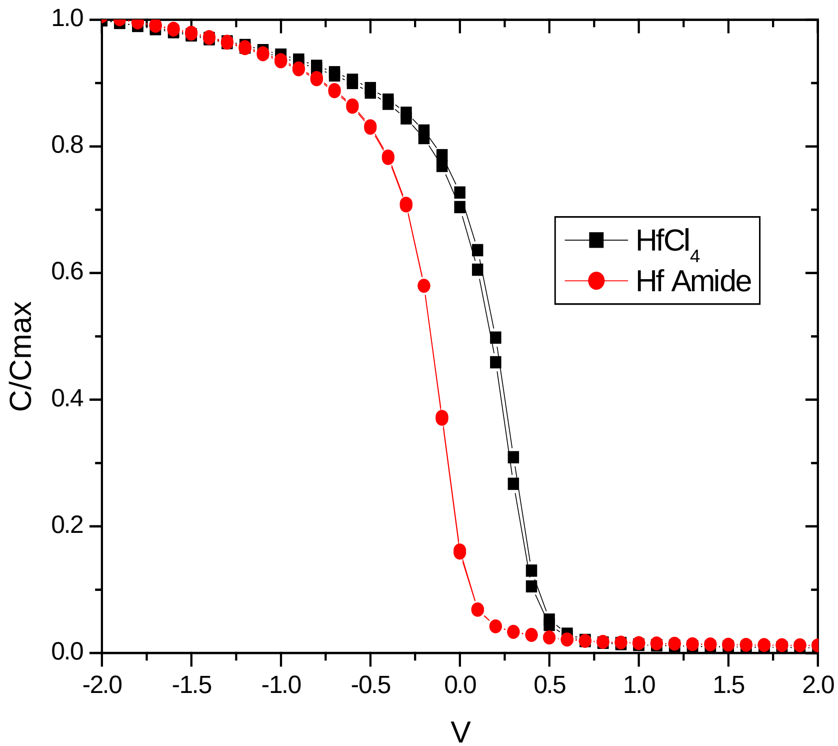
TEM x-section

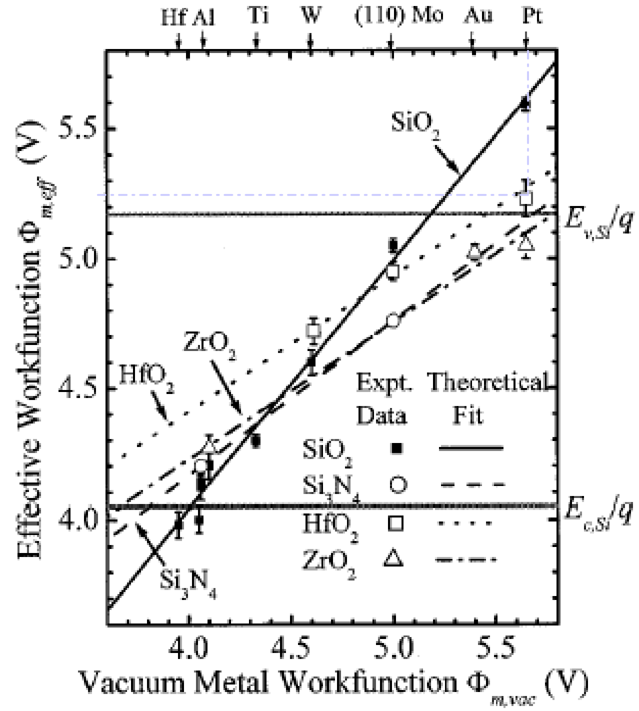


x-section TEM image shows a uniform amorphous HfO_2 film deposited on chemical oxide.

HfO_2 thickness = 45Å
I.L (chem ox) = 15Å

Effect of Precursor on V_{FB}





V_{FB} (alkylamide) = 0.09V
V_{FB} (chloride) = 0.49V

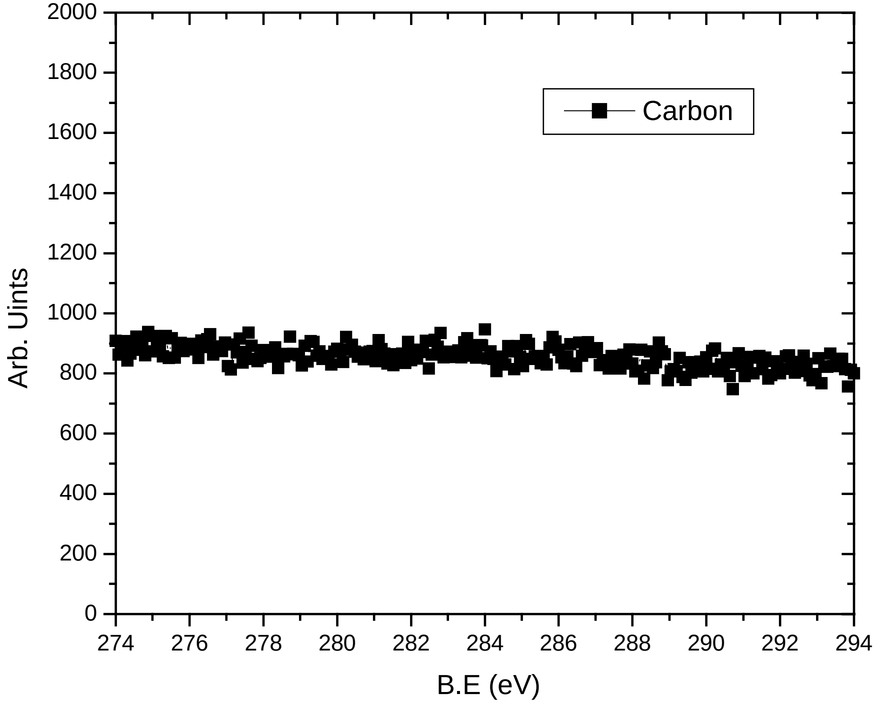
(Yee-Chia Yeo, *et. al. IEEE EDL, 2002*)

Q_F (alkylamide) = + 2.4E12
Q_F (chloride) = -1.29E12

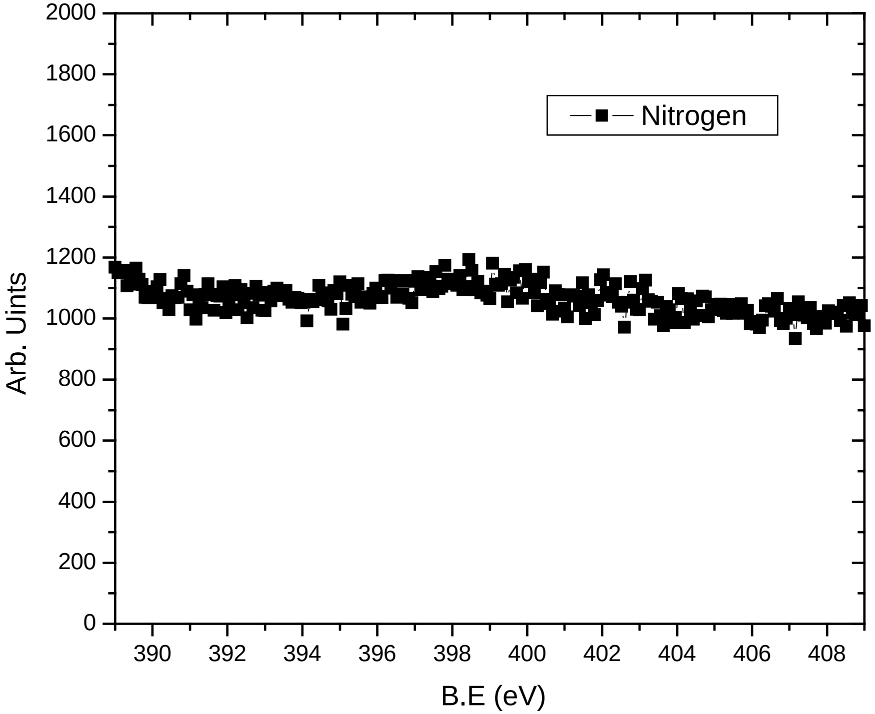
ϕ_{Pt} = 5.25 eV on HfO_2
"Ideal" V_{FB} = 0.35V

Impurities in HfO_2

Carbon Signal

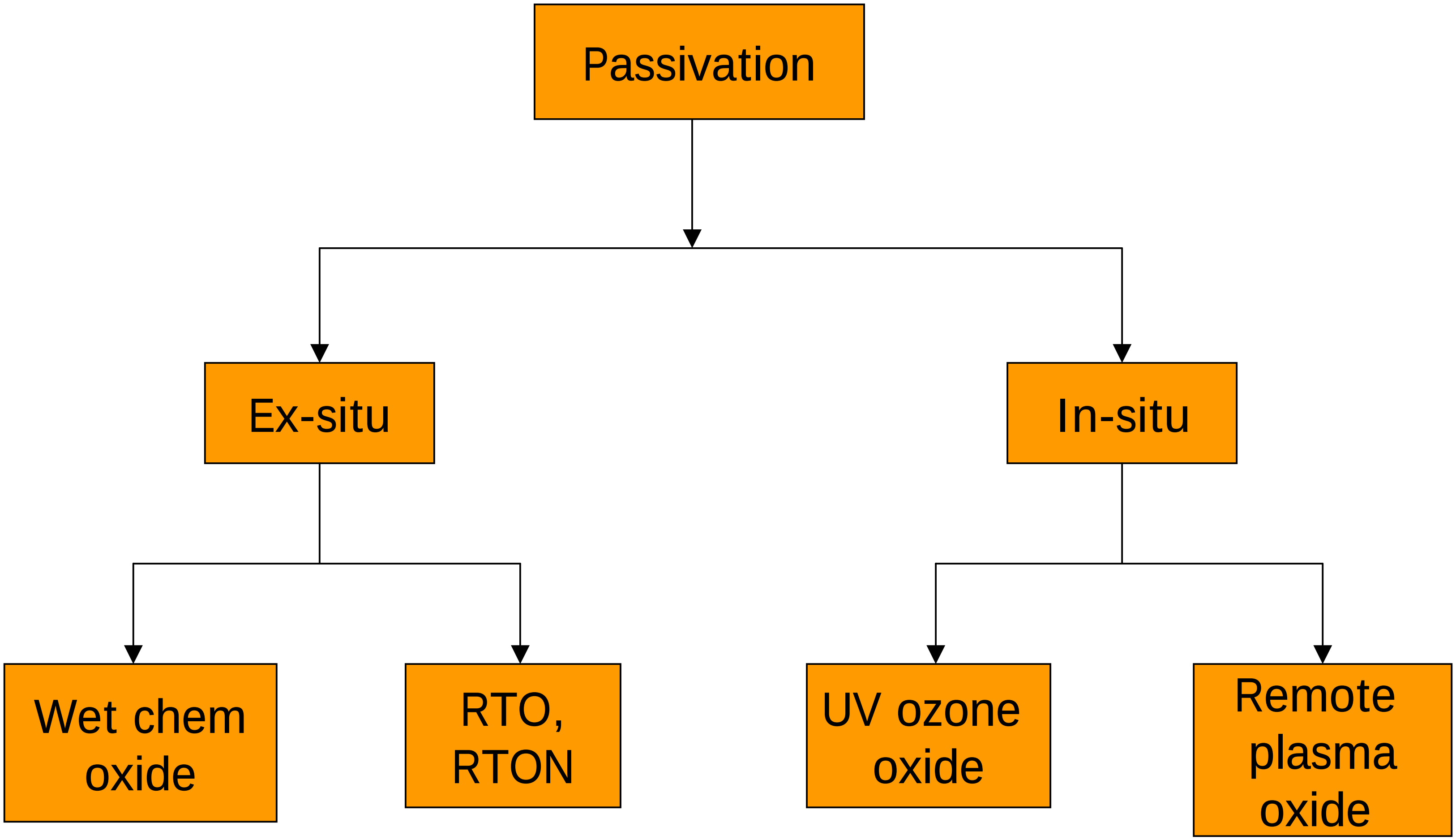


Nitrogen Signal



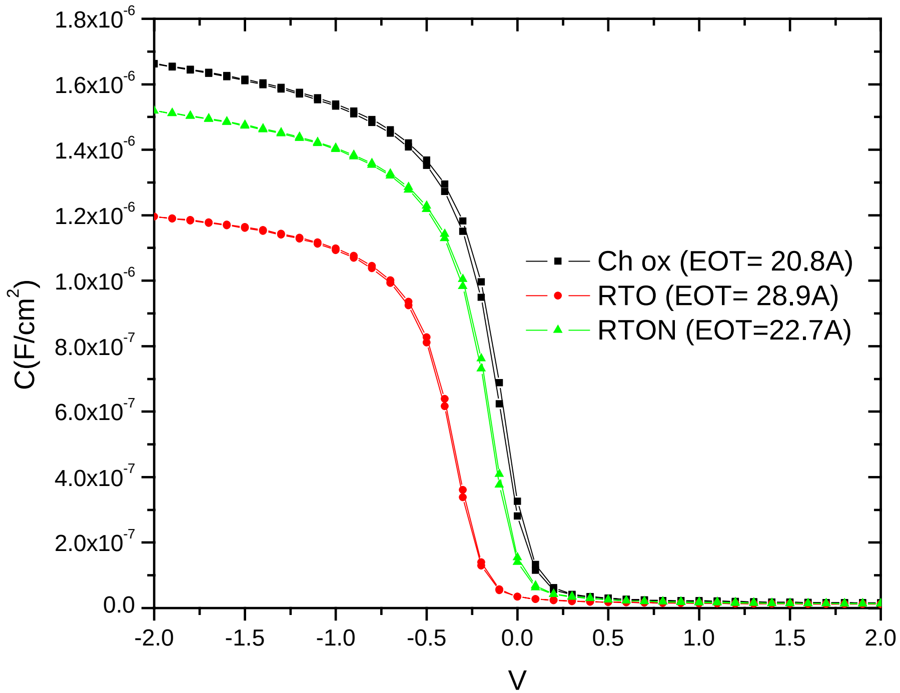
Carbon and nitrogen impurities were below the detection levels of the XPS. In comparison, 1-2 atomic % Cl was typically detected from as-grown $HfCl_4$-derived films.

Templates for ALD

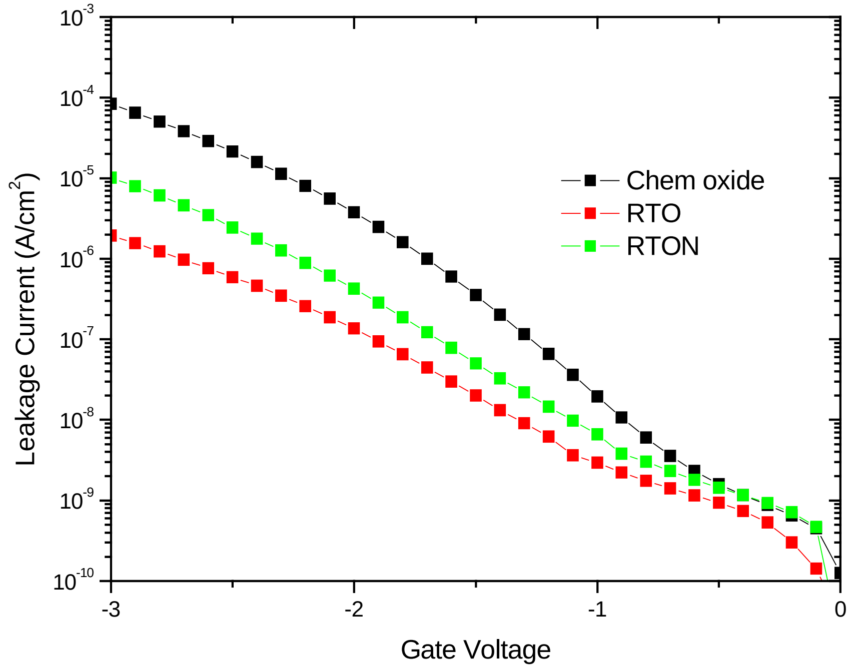


Electrical Characteristics

C-V Characteristics



Leakage Current



50Å HfO_2 was deposited on the Chem Ox (15Å), RTO (20Å) and RTON (20Å) samples.

The electrical results indicate an excellent quality HfO_2 with very low leakage current.

Summary and Future Work

Summary

- We have successfully grown high quality HfO_2 thin films on silicon substrates using the ALD process.

- The electrical characteristics of the HfO_2 films grown using TDEAH are far superior to those obtained using the chlorides.

- The carbon and nitrogen impurity levels in the films were below the detection limits of the XPS.

- The low substrate temperature for the alkylamide process will facilitate area selective ALD on patterned substrates.

Future Work

- Study the crystallization kinetics of ALD HfO_2 grown using TDEAH.

- Optimize the ALD TaN process for in-situ gate electrode deposition