

# ***Understanding Atomic Layer Deposition (ALD) of $ZrO_2$ and $HfO_2$ Using Density Functional Theory***

Joseph H. Han,<sup>a</sup> Yuniarto Widjaja,<sup>a</sup> Rong Chen,<sup>b</sup> Stacey F. Bent,<sup>a</sup> Roy G. Gordon,<sup>d</sup> Guilian Gao,<sup>e</sup> and Charles B. Musgrave<sup>a,c</sup>

*<sup>a</sup>Departments of Chemical Engineering, <sup>b</sup>Chemistry, and <sup>c</sup>Materials Science and Engineering, Stanford University, Stanford, CA 94305*

*<sup>d</sup>Harvard University Chemical Laboratories, Cambridge, MA 02138*

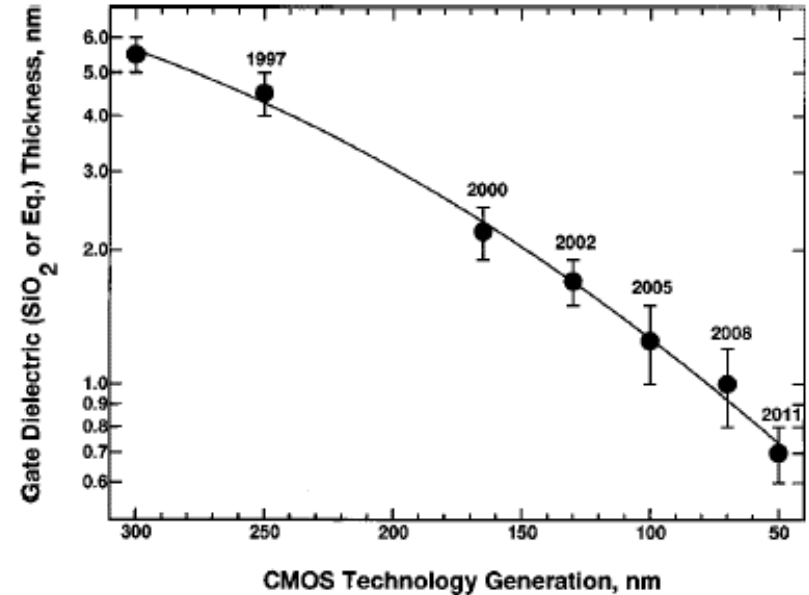
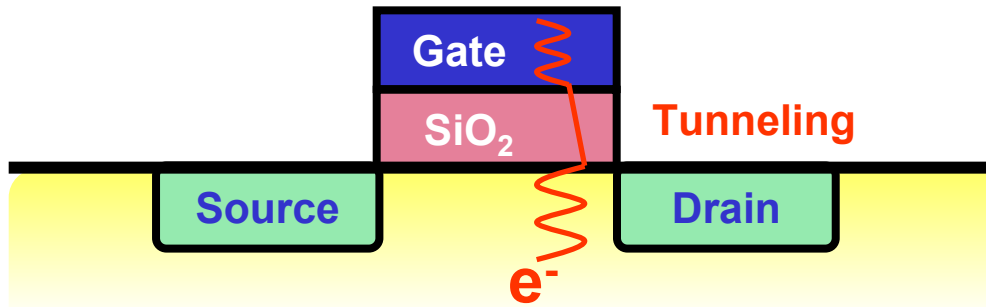
*<sup>e</sup>Materials Science Department, Ford Research Laboratory, Ford Motor Company, Dearborn, MI 48121*



# CMOS Gate Leakage Due to Electron Tunneling

## Current Transistor Technology:

- Leakage current from electron tunneling increasing exponentially as gate dielectric thickness decreases.



Green at al., J. Appl. Phys, 2001, adapted from ITRS

## ITRS Executive Summary: Challenging Issues Through 2007

1. Cost effectiveness, process control, and reliability of very thin oxy-nitride **gate dielectrics**, especially considering the **high gate leakage**.
4. Controlling static power dissipation in the face of **rapidly increasing leakage**.
6. Early availability of manufacturing-worthy **high-k gate dielectrics** is necessary to meet stringent **gate leakage** and performance requirements.

$$C = \frac{k\epsilon_0}{t}$$



# High-K Choices

Dielectric Materials		$\kappa$
silicon oxide	$\text{SiO}_2$	3.5
silicon nitride	$\text{Si}_3\text{N}_4$	7
aluminum oxide	$\text{Al}_2\text{O}_3$	9
zirconium oxide	$\text{ZrO}_2$	25
hafnium oxide	$\text{HfO}_2$	30 - 40

- $\text{ZrO}_2$ ,  $\text{HfO}_2$ , and  $\text{Al}_2\text{O}_3$  are favorable candidates for the gate dielectric
  - High- $\kappa$
  - Stable with respect to  $\text{SiO}_2$  and silicate formation
- **Problem:** Process for producing uniform films with good dielectric properties needs to be developed.
  - Possible solution: Atomic Layer Deposition (ALD)
- **Problem:** Need interface with good electrical properties
  - Possible solution: Deposit one atomic layer of  $\text{SiO}_2$



# The ALD Process

## Self-terminating Reactions

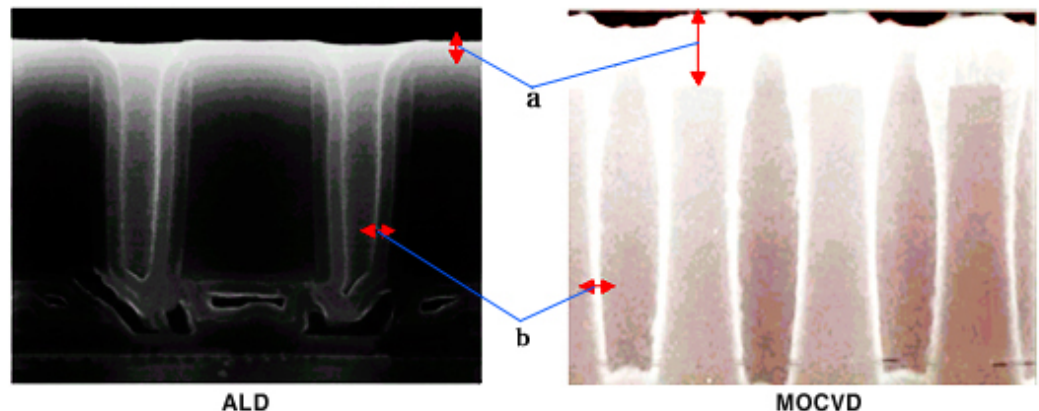
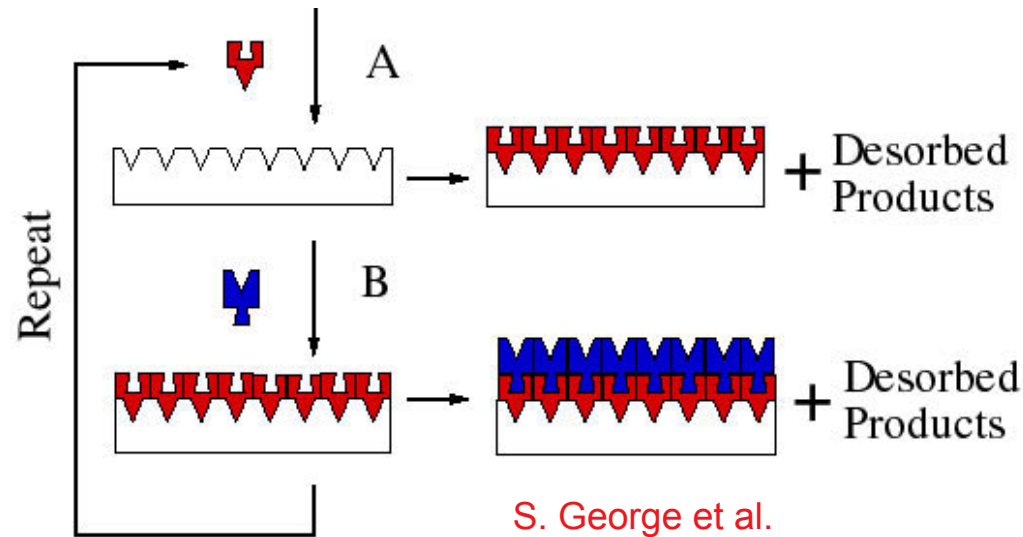
- ALD consists of an alternating sequence of self-terminating reactions.
- **Ideally, each step should form a monolayer.**

## Advantages of ALD

- Excellent conformality (step coverage >95%)
- Excellent film thickness control –allows for growth of extremely thin films
- Low processing temperatures
- High purity films
- **Selective ALD could reduce raw material requirements and by-product generation**

## ALD Issues

- Process is slow
- **Submonolayer** coverage
- Interlayer SiO<sub>2</sub> below ZrO<sub>2</sub>



$$\text{Step Coverage} = \frac{b}{a} \times 100(\%)$$

TEM micrographs of Al<sub>2</sub>O<sub>3</sub> obtained with ALD and conventional MOCVD process (courtesy of IPS-Tech)



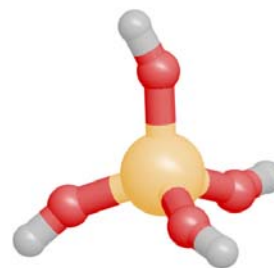
# Computational Details

Gaussian 98 is used for the density functional theory (DFT) calculations.

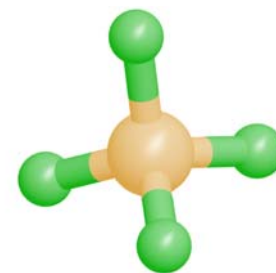
The B3LYP method is used in conjunction with LANL2DZ basis sets on Zr, Hf, Si, and Cl atoms. The remainder of the atoms (H, C, N, and O) are described using a D95(d,p) basis set.

Frequency calculations are done to characterize stable and transition state structures and to determine zero point energies and thermal corrections.

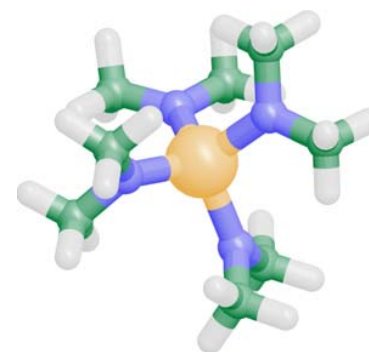
Clusters were used to simulate the surface reacting with gas phase molecules. Sensitivity studies with respect to cluster size ensure that the chemistry is captured.



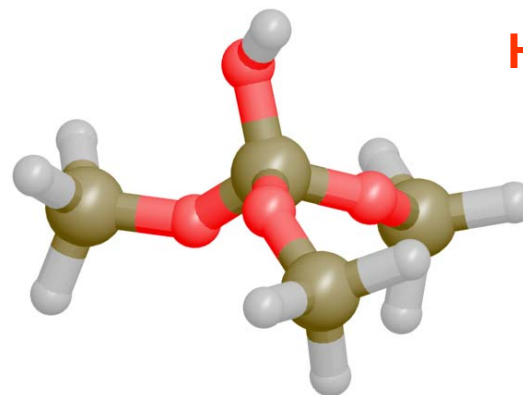
$X(OH)_4$   
 $X=Zr \text{ or } Hf$



$XCl_4$   
 $X=Zr \text{ or } Hf$



$Hf(N(CH_3)_2)_4$



$SiO_2$  surface cluster



$H_2O$

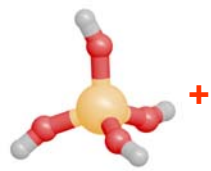


$HCl$

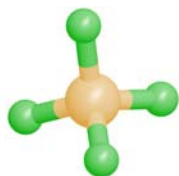


# ZrO<sub>2</sub> ALD Reaction with Zr-OH\* Sites

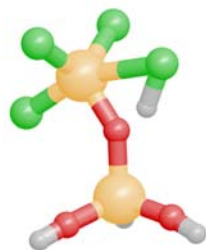
Reactants



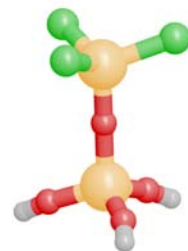
+



ZrCl<sub>4</sub>(g)



Products

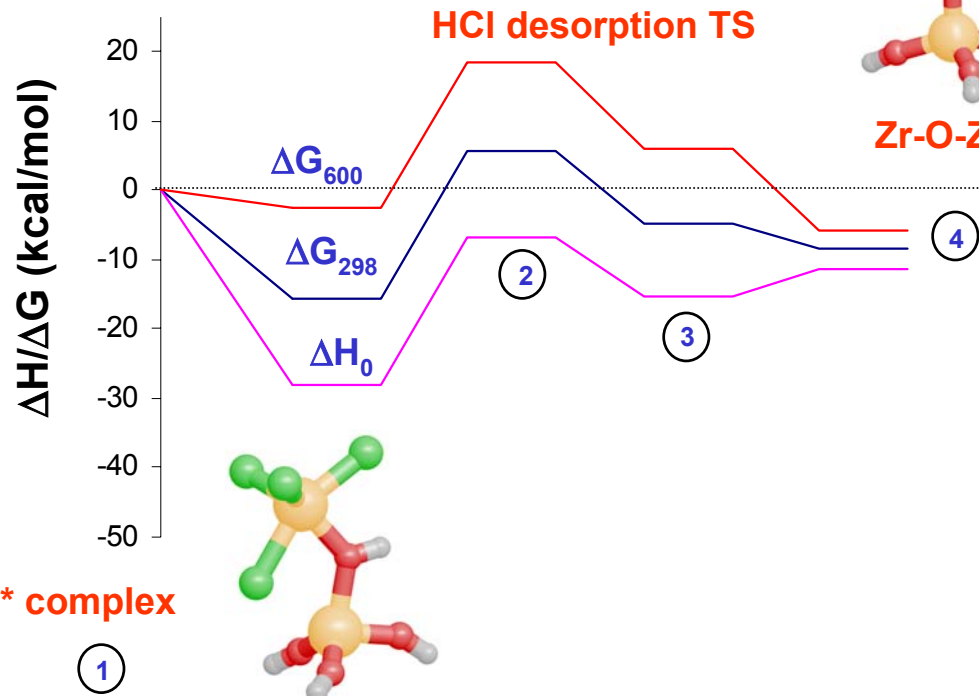


Zr-O-ZrCl<sub>3</sub>\*

+



HCl(g)

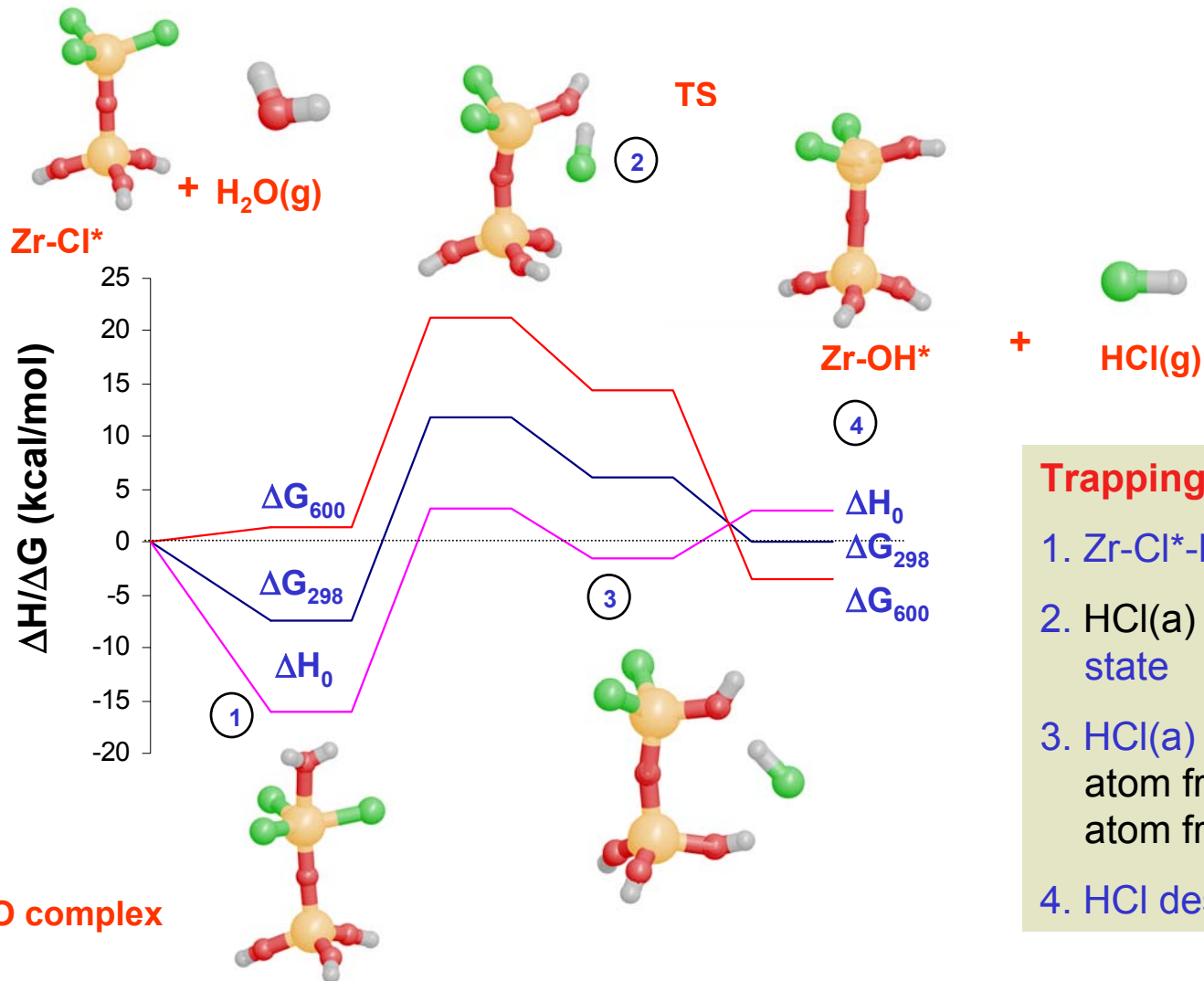


**Trapping-mediated pathway:**

1. Zr-OH\*-ZrCl<sub>4</sub> complex is formed
2. HCl(a) formation transition state
3. HCl(a) is formed from one H atom from H<sub>2</sub>O and one Cl atom from ZrCl<sub>3</sub>
4. HCl desorbs



# ZrO<sub>2</sub> ALD Reaction with Zr-Cl\* Sites

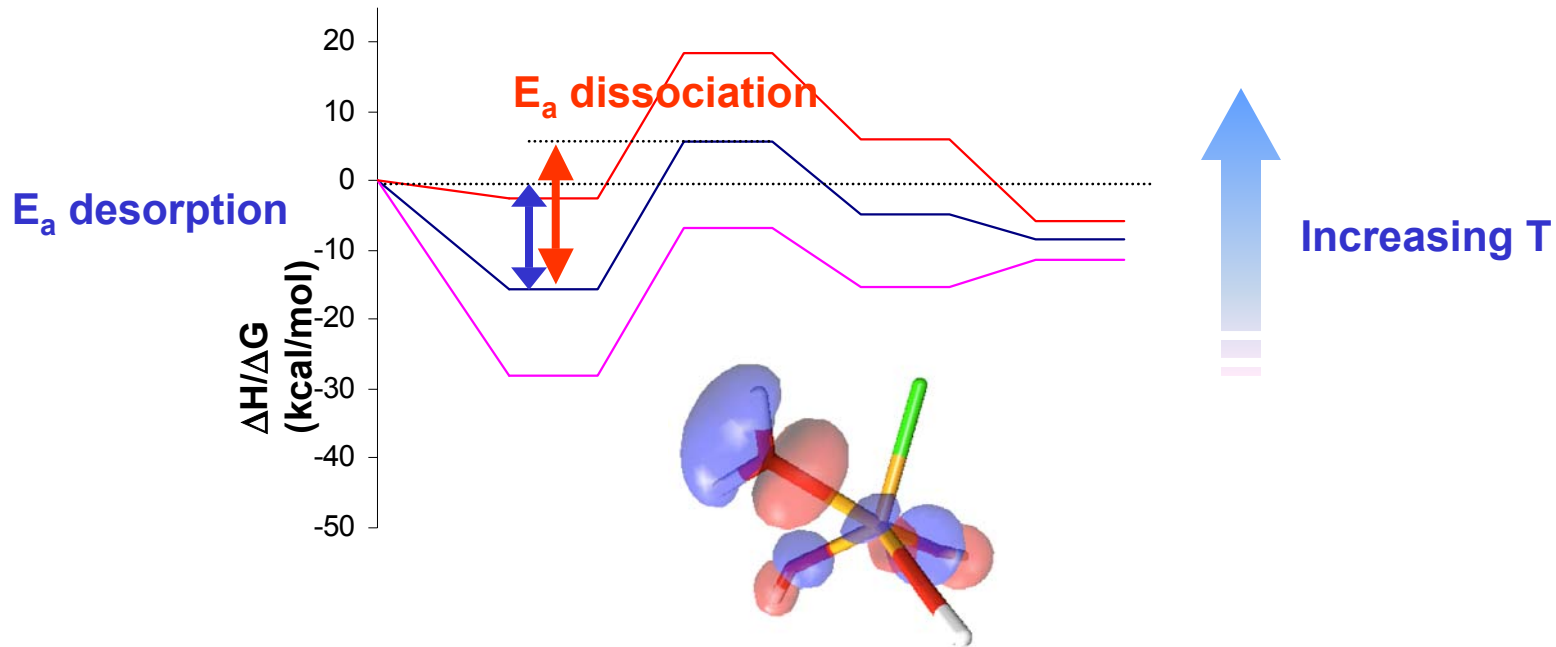


## Trapping-mediated pathway:

1. Zr-Cl\*-H<sub>2</sub>O complex is formed
2. HCl(a) formation transition state
3. HCl(a) is formed from one H atom from H<sub>2</sub>O and one Cl atom from ZrCl<sub>3</sub>
4. HCl desorbs



# Partial Monolayer Growth



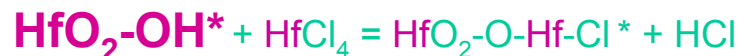
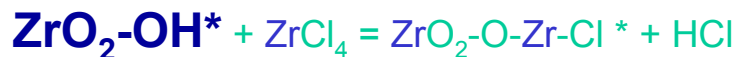
- Raising the temperature raises new issues:
  - Desorption becomes more favorable than dissociation
  - This results in **less than a monolayer coverage** per cycle.
  - Low-thermal budget processing might be desired



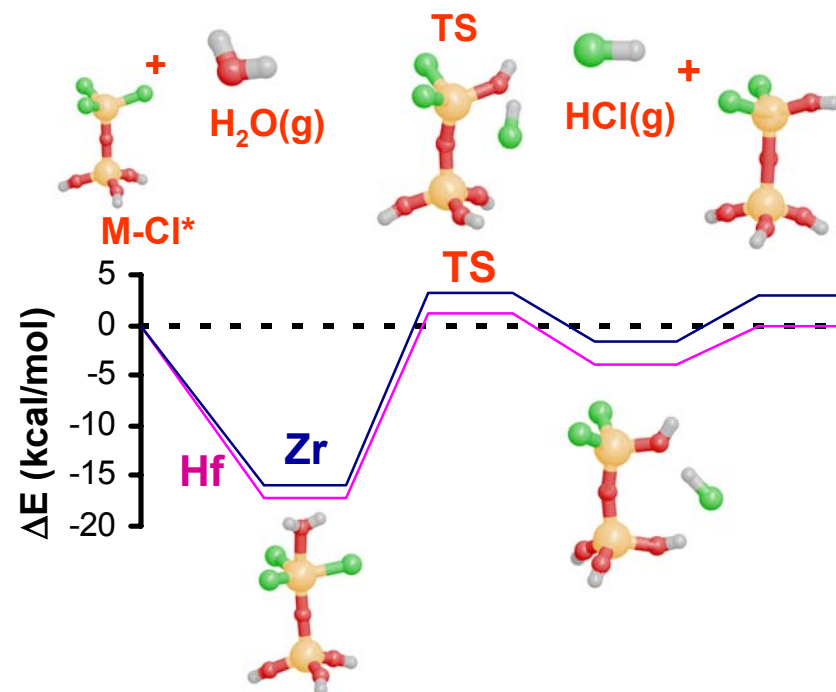
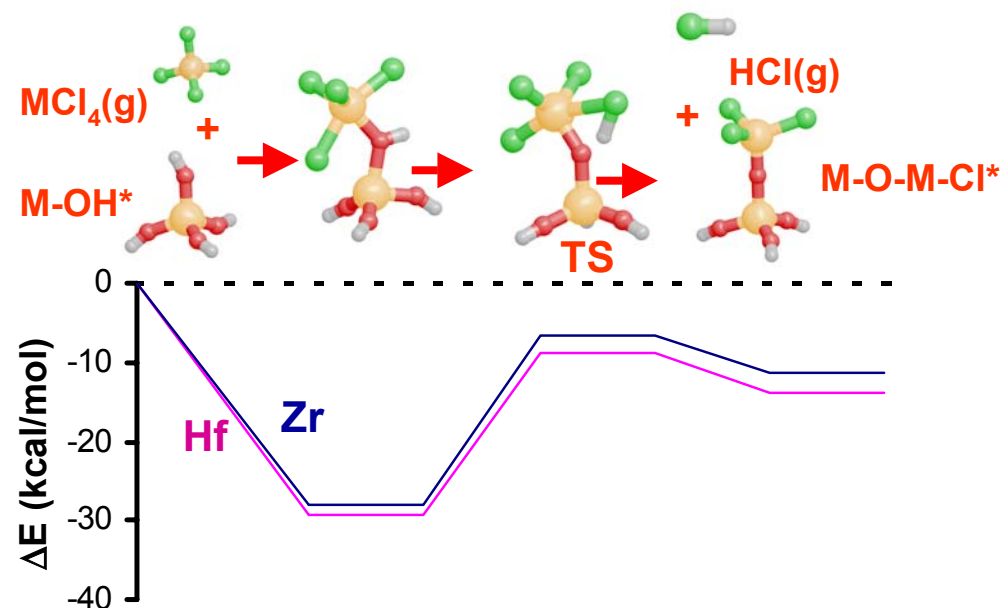


# Comparison of $ZrO_2$ and $HfO_2$ ALD Reactions using $M-Cl_4$

## Half-reaction with $MCl_4$ :



## Half-reaction with $H_2O$ :



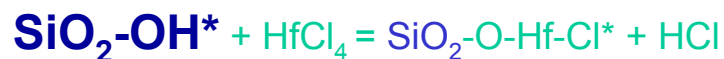
Qualitatively similar reaction paths because the chemical reactions are very localized.

Issues: Trapping at the intermediate state.

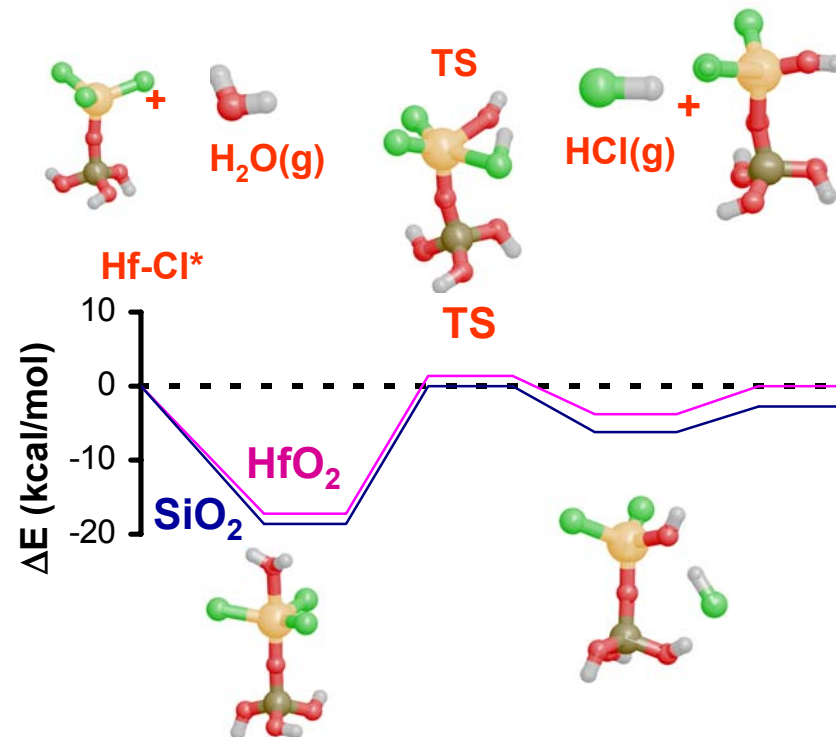
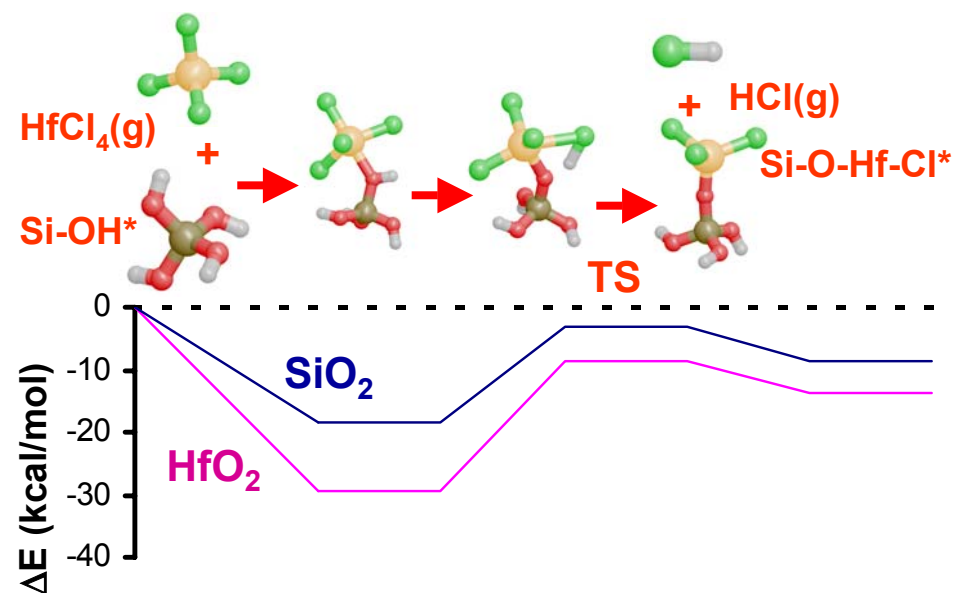
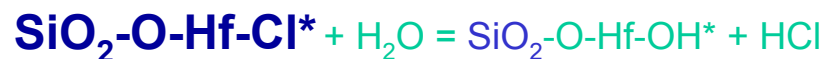


# Comparison of $\text{HfO}_2$ ALD Reactions on $\text{SiO}_2$ and $\text{HfO}_2$

## Half-reaction with $\text{HfCl}_4$ :



## Half-reaction with $\text{H}_2\text{O}$ :



Qualitatively similar reaction paths because the chemical reactions are very localized.

Issues: Trapping at the intermediate state.

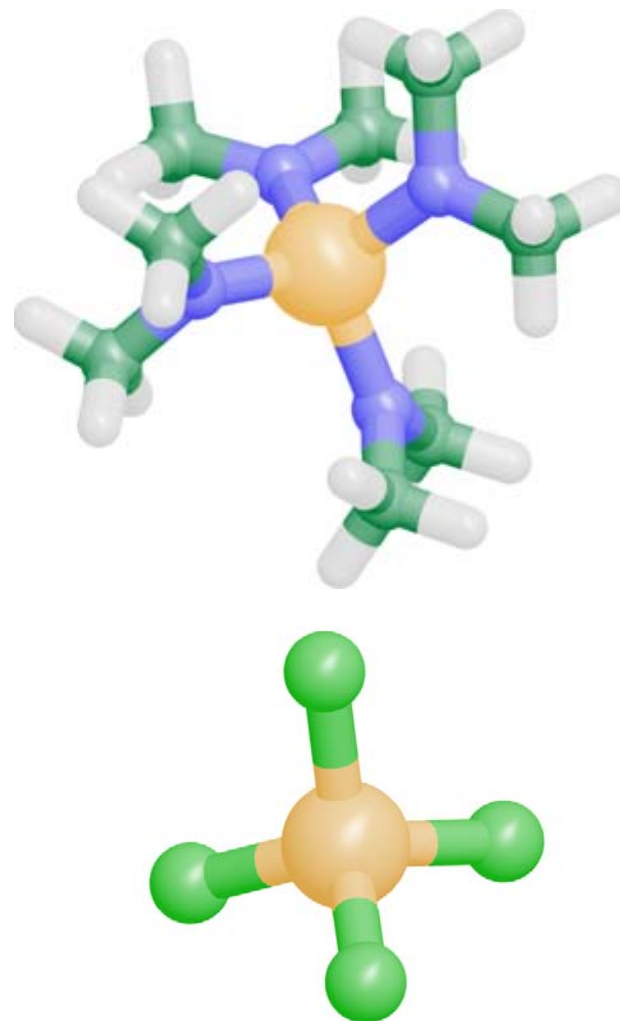


# Alternative Precursor - Alkylamides

- Size is slightly larger than metal-chlorides
  - Should **worsen** submonolayer growth rate if it is a steric effect
- Experimentally, improved growth rates at lower temperatures are observed (Hausmann, et al., 2002)

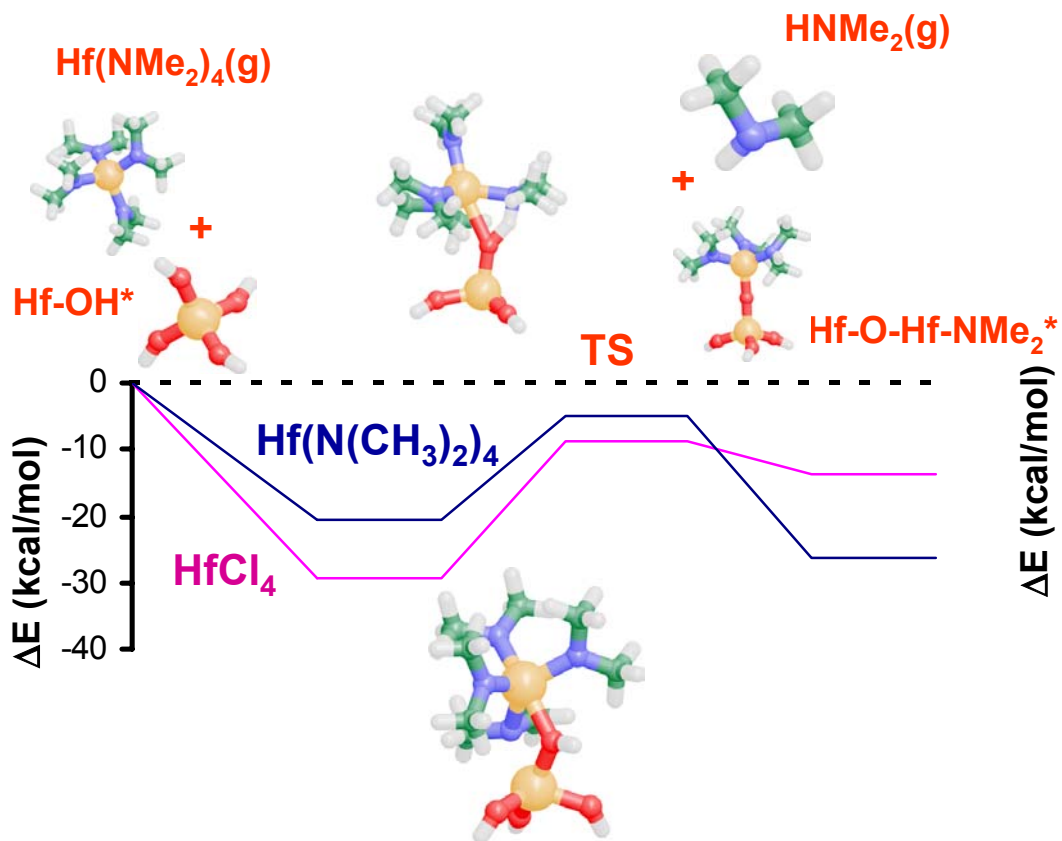
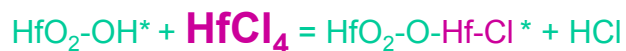
## Additional Benefits

- Better volatility compared with metal-chlorides because of the hydrocarbon shell
  - Effect is enhanced with longer alkyl chains (ethyl versus methyl)
- The alkylamine by-products are easier to handle than HCl

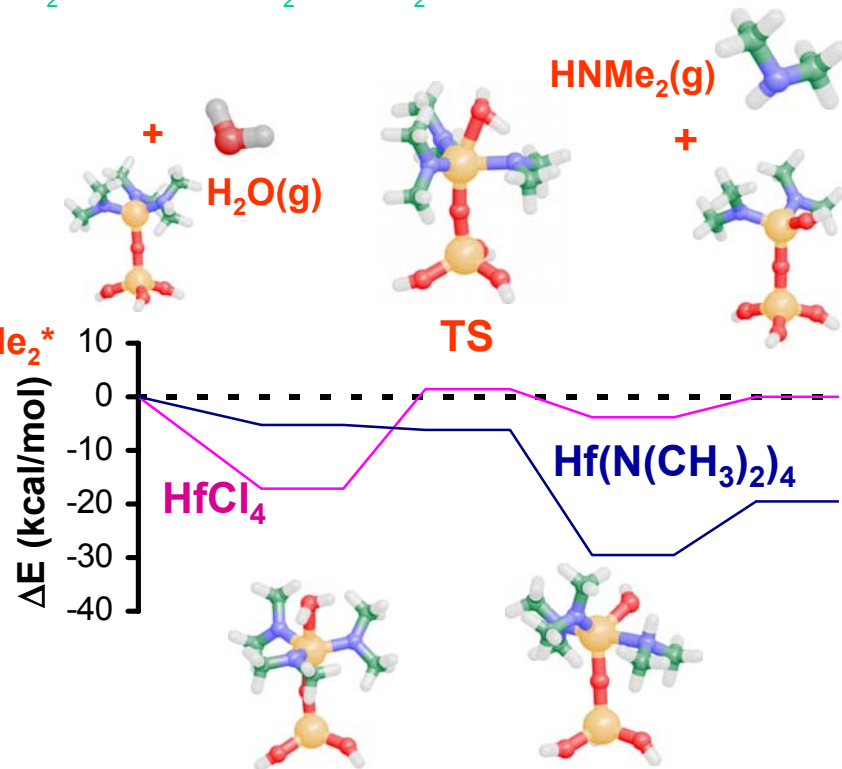
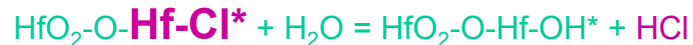
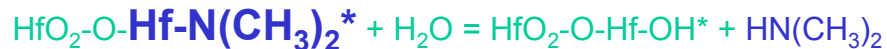


# HfO<sub>2</sub> ALD Reactions using Hf(NMe<sub>2</sub>)<sub>4</sub> versus HfCl<sub>4</sub>

## Half-reaction with Hf(X)<sub>4</sub>:



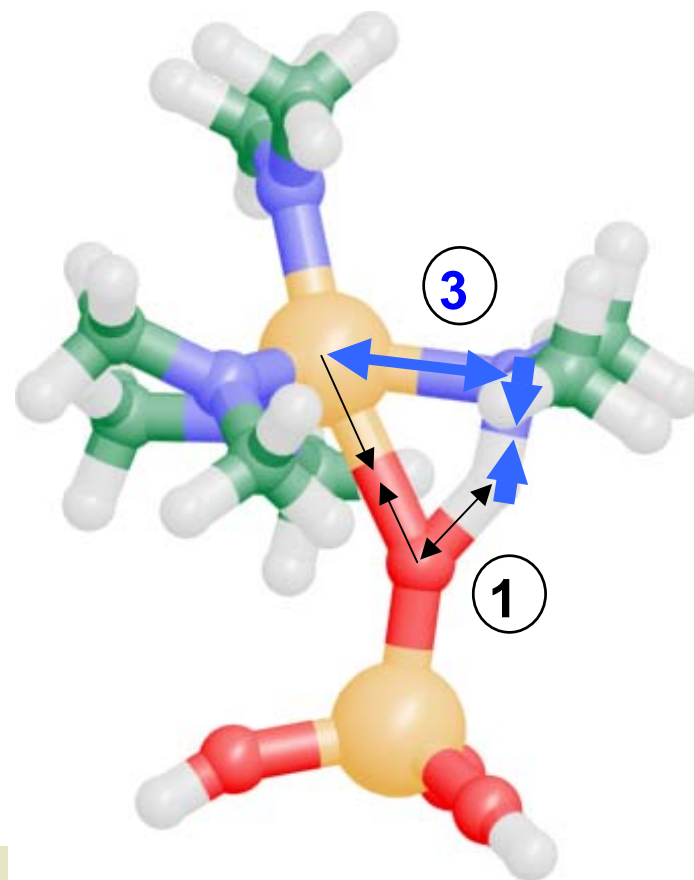
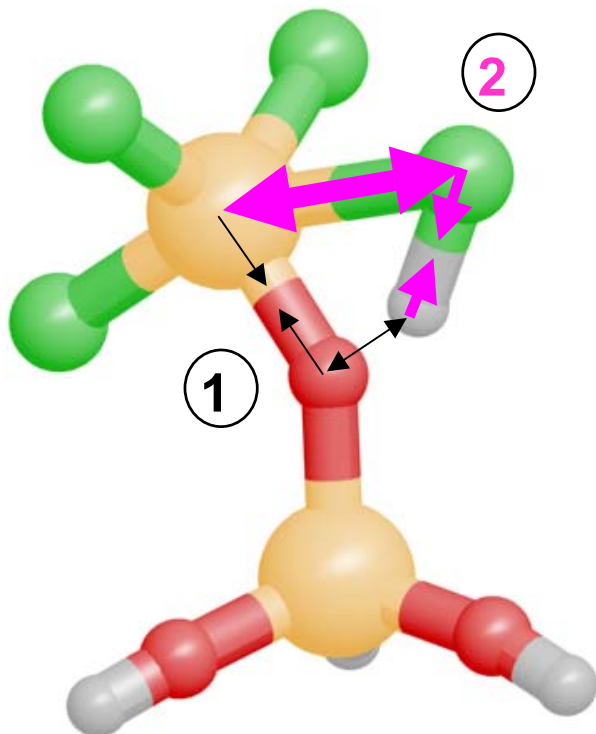
## Half-reaction with H<sub>2</sub>O:



Hf(N(CH<sub>3</sub>)<sub>2</sub>)<sub>4</sub> reaction is exothermic and does not exhibit trapping of intermediate state.



# Thermodynamic Effects



1. Hf-O bond formed and O-H bond broken in both cases
2. Broken bond is stronger relative to formed bond in **Metal-chloride** case
3. Formed bond is stronger relative to broken bond in **Metal-alkylamine** case

Bond Energies (kcal/mol)			
	OH	Cl	N(CH <sub>3</sub> ) <sub>2</sub>
H-X	114.22	95.04	91.52
Hf-X <sub>4</sub>	121.09	103.51	81.03



# HfO<sub>2</sub> ALD Reactions -- Orbitals

Energies given in hartrees; 1 hartree = 627.5095 kcal/mol

E=-0.073 [LUMO] E=-0.002

E=-0.326 [HOMO] E=-0.196

E=-0.329 [HOMO-1] E=-0.206

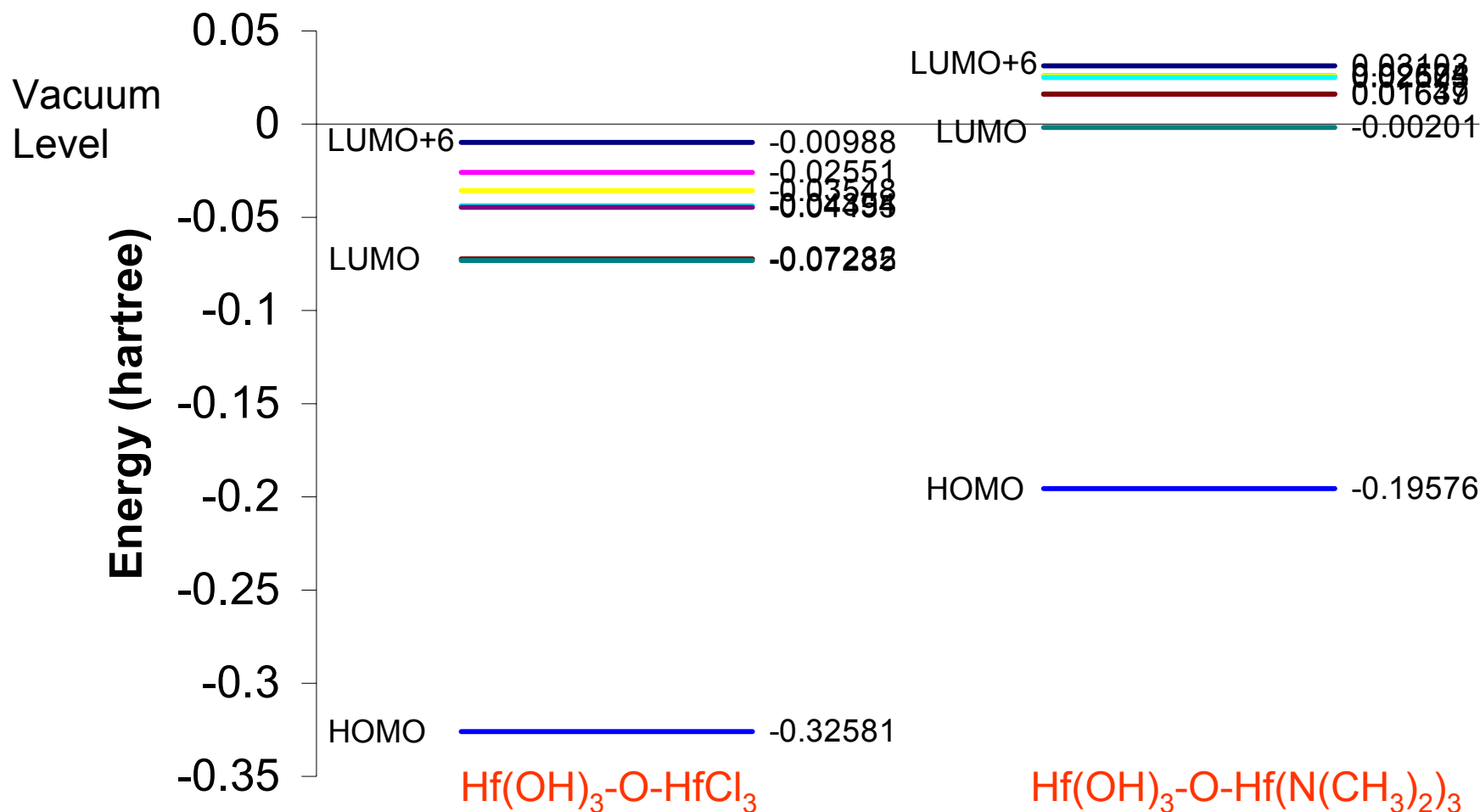
HfCl<sub>4</sub> Precursor

Hf(N(CH<sub>3</sub>)<sub>2</sub>)<sub>4</sub> Precursor

Hf-O-Hf(NMe<sub>2</sub>)<sub>3</sub> has an electron cloud "halo" preventing a trapped water intermediate.



# Orbital Energies

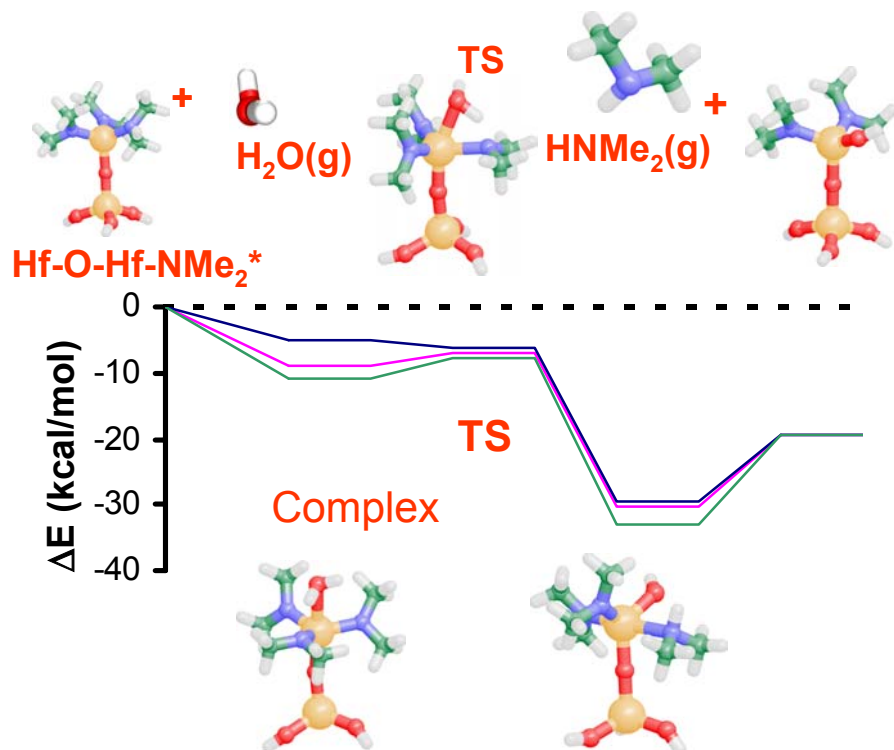


1.  $\text{-HfCl}_3$  reaction site has 7 unoccupied orbitals below the vacuum level localized about the reactive Hf atom.
2.  $\text{-Hf(N(CH}_3)_2)_3$  reaction site has 1 unoccupied orbital below the vacuum level. Only LUMO+1 and higher have orbitals localized about the reactive Hf atom.



# Second HfO<sub>2</sub> ALD Half Reaction with $-HfOH_x(N(CH_3)_2)_{3-x}$

## Half-reaction with H<sub>2</sub>O:



- As -OH groups replace -NMe<sub>2</sub>, the “halo” gradually disappears. More stable H<sub>2</sub>O complex.
- Second half reaction for ALD of HfO<sub>2</sub> is still favorable even after -OH substitution of -N(CH<sub>3</sub>)<sub>2</sub>





# Conclusions

**Metal-chloride** ( $MCl_4$ ,  $M=Zr$  or  $Hf$ ) precursors have strongly bound complexes and **require thermal energy** to overcome the reaction barrier. However, at higher temperatures, **desorption is favored** over reaction. Combined with the fact that the reaction is **endothermic** relative to the initial complexes, **submonolayer growth rates** are observed experimentally.

**Metal-alkylamide** (e.g.  $Hf(N(CH_3)_2)_4$ ) precursors do not have the strongly bound water complex because of an **electron density “halo”** preventing electron donation. Furthermore, the relative energies of the bonds being formed and broken are such that an **exothermic** reaction is expected. Therefore, **improved growth rates** are predicted which corroborate with experimental observations.

## Acknowledgements

Powell Foundation, IBM, Hewlett-Packard, LSI Logic, Semiconductor Research Corporation (SRC), National Science Foundation (NSF), National Center for Supercomputer Applications (NCSA)

