

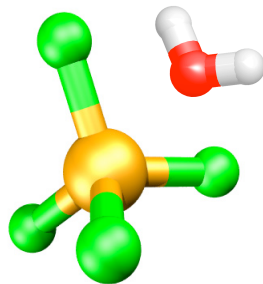
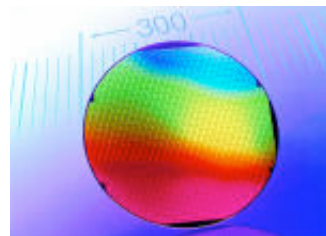
The Chemistry of ALD of High-K Dielectrics

Selection of Precursors, and Substrates

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Stanford University, Stanford, CA



Design of new processes that are environmentally benign can be greatly aided by an understanding of the process chemistry



Why Do Simulation ?

As technology proceeds to the **nanoscale regime** and **new materials** are introduced, it is increasingly critical to **develop simulation capabilities**:

- for **robust process design** and to design benign characteristics into processes ab initio
- to **guide experimental** work
- to investigate new and radical **alternatives** beyond experimental capabilities
- to provide an **intellectual framework** for the education of future technology workers

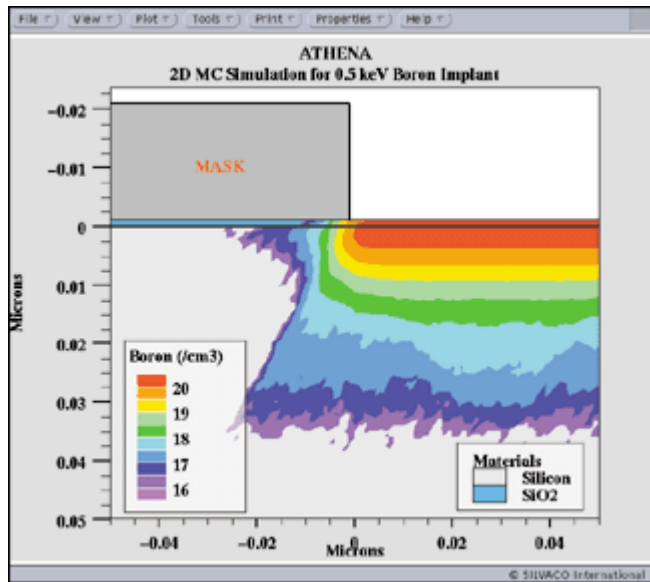
“Modeling and simulation is the “glue” necessary to connect all the elements of future technology development”

SRC Consultative Working Group - Multiscale/Multi Phenomena Modeling and Simulation



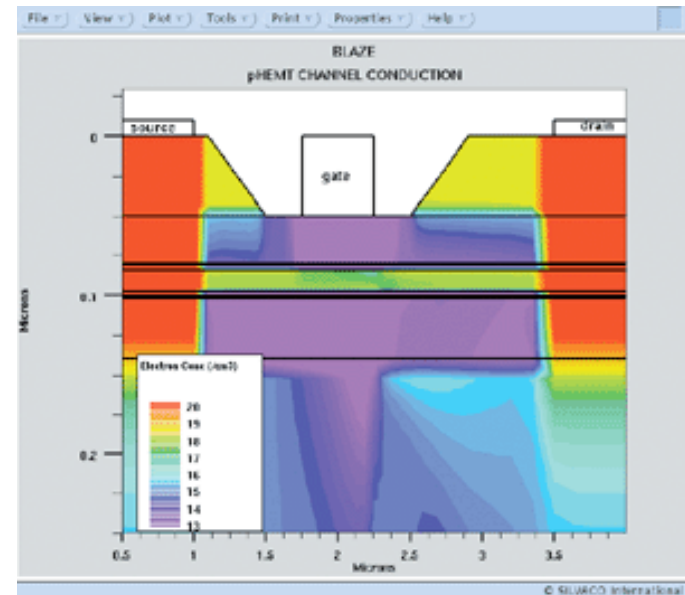
Traditional TCAD

Process Simulation



www.silvaco.com

Device Simulation

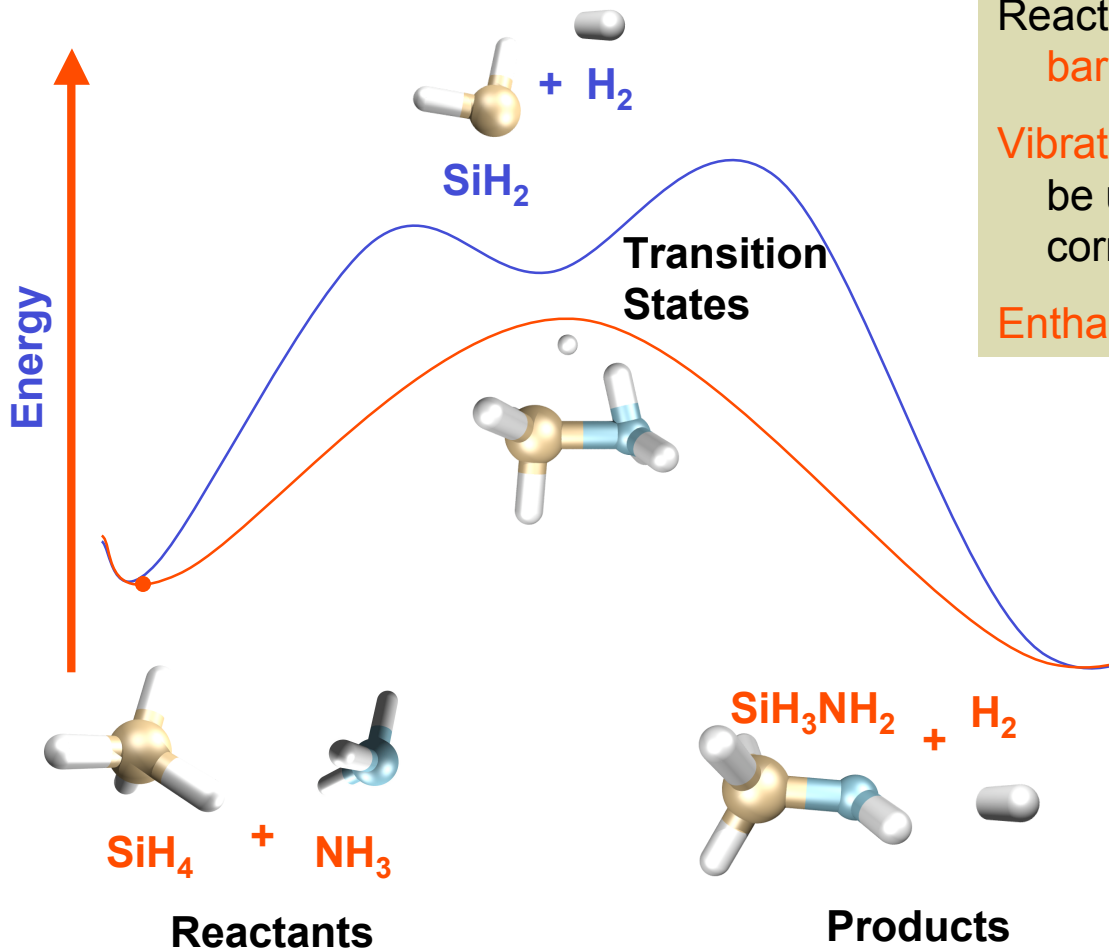


TCAD has been successfully implemented to **computationally prototype processes** such as oxidation, ion implantation, and dopant profile evolution. However, **development of film deposition and etch processes** still remains predominantly **empirical**. Models that are developed are extrapolations and do not contain detailed chemical kinetics and lack basic details of the surface chemistry.



Chemistry of Electronic Materials

Which pathways are active and what are their rates?



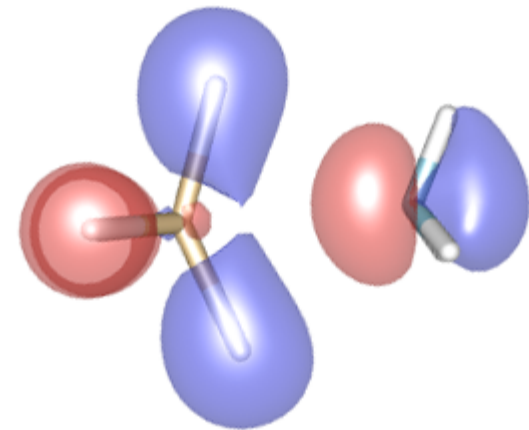
Reactants and products are local minima.

Transition states are saddle points.

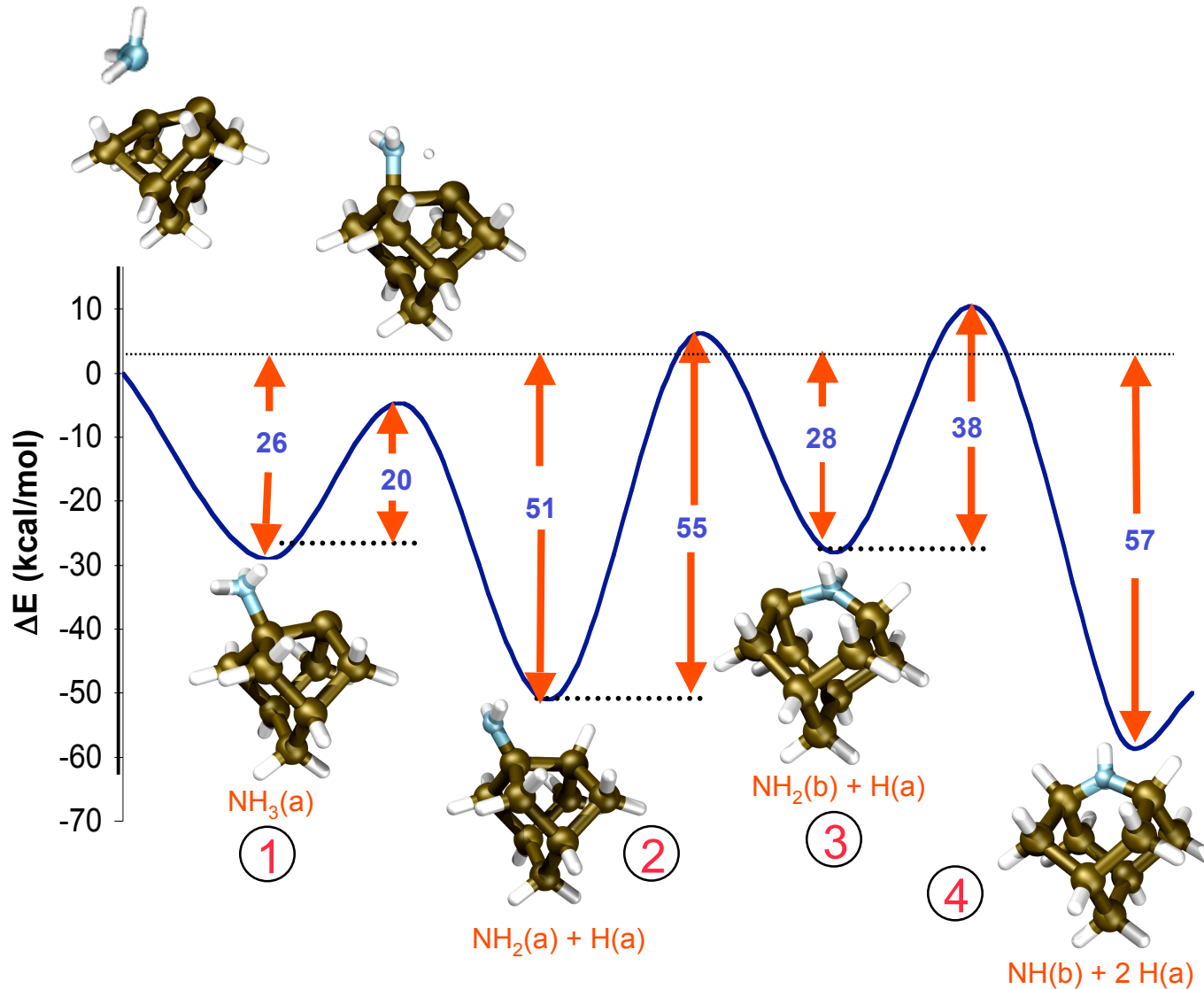
Reaction rate a function of the activation barrier and temperature

Vibrational frequencies can identify species, be used for zero-point and thermal corrections, and pre-exponential factors.

Enthalpy of Reaction driving force for rxn



NH_3 on $Si(100)-(2 \times 1)$



Insertion Mechanism:

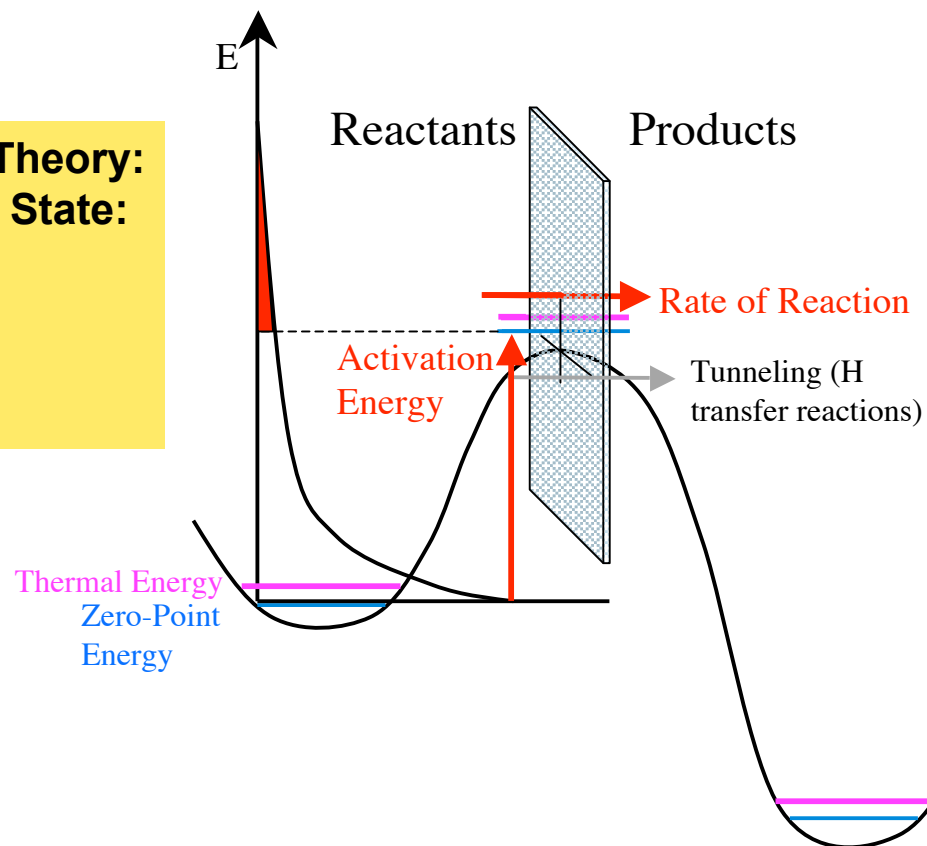
1. $NH_3(g)$ initially adsorbs on the “down” Si atom.
2. $NH_3(a)$ dissociates into $NH_2(a)$ and $H(a)$.
3. $NH_2(a)$ inserts into Si-Si dimer bond.
4. $NH_2(a)$ dissociates into $NH(a)$ and $H(a)$.

- Insertion barrier is higher than desorption barrier.
- TPD (Chen, 1992)
 - 73% of $NH_2(a)$ species recombine with $H(a)$



Predicting Reaction Rates

Input for Transition State Theory:
Initial state and Transition State:
Structures
Rotational inertia
Energies
Vibrational frequencies



Rate Equation

$$K = \frac{kT}{h} \frac{q^{TS}}{q_A q_B} \exp\left[-\frac{E_a}{RT}\right]$$

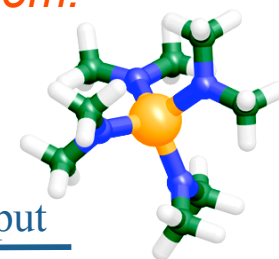
Partition Functions

$$Z = \sum_i g_i \exp\left[-\frac{E_i}{RT}\right]$$



What is Quantum Chemistry?

Quantum chemistry is a set of methods developed for solving the Schrodinger equation to determine the electronic structure of a system.



Input

Nuclear Coordinates,
n and s.

The Hamiltonian:

$$\hat{H} = -\sum_i \frac{\hbar^2 \nabla_i^2}{2m} - \sum_{i,A} \frac{Z_A e^2}{r_{iA}} + \sum_{i,j>i} \frac{e^2}{r_{ij}} + \sum_{A,B>A} \frac{Z_A Z_B e^2}{R_{AB}}$$

The Schrödinger equation

$$\hat{H}|\psi\rangle = E|\psi\rangle$$

A lot of math and approximations

$$\psi(1,2,\dots,n) = \begin{matrix} \xrightarrow{\text{n orbitals}} \\ \begin{vmatrix} \phi_1(x_1) & \phi_2(x_1) & \dots & \phi_n(x_1) \\ \phi_1(x_2) & \phi_2(x_2) & \dots & \phi_n(x_2) \\ \dots & \dots & \dots & \dots \\ \phi_1(x_n) & \phi_2(x_n) & \dots & \phi_n(x_n) \end{vmatrix} \\ \downarrow \text{n electrons} \end{matrix}$$

The Variational Principle

$$\frac{\partial}{\partial c_i} \langle \psi | \hat{H} | \psi \rangle = 0$$

Basis functions

$$\phi_j = \sum_i^k c_i \varphi_i$$

Basis functions



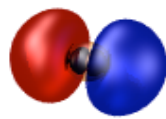
1s



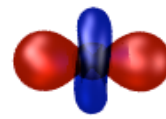
2s



3s



3p_x



3d_{z²}



3d_{xy}

...



Typical Errors for QC Methods

For a set of 40 reactions with reliable “experimental” barriers and enthalpies of reaction we obtain the following RMS and maximum errors:

	Barriers		Enthalpies	
	RMS Error	MAD	RMS Error	MAD
B3LYP (3)	3.59	10.8	2.25	7.01
G2 (7)	3.3	10.1	1.26	7.51
CCSD(T) (7)	2.61	4.4	1.4	3.6
KMLYP (3)	1.3	4.2	1.4	3.5
CBS-APNO (8)	1.26	4.4	1.2	3.3

Energies is kcal/mol

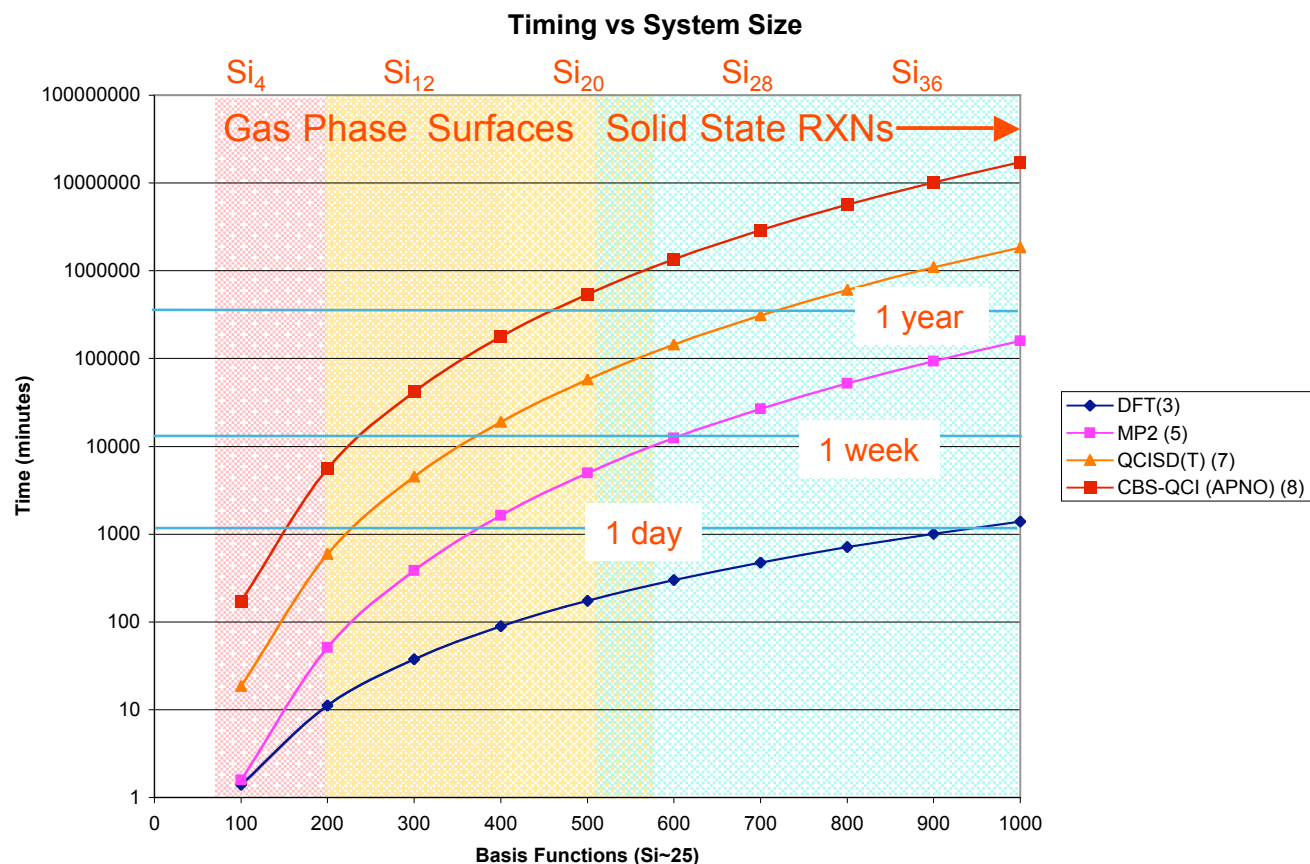
- *CCSD(T) limited to systems with 8-10 atoms.*
- *CBS-APNO is limited to systems with only 3 to 4 atoms.*
- *B3LYP and KMLYP can simulate systems of more than 50 atoms.*



Computational Cost

Single-point energy calculations. Run on 1 processor of 128 processor (2GHz Athlon) cluster.

Geometry optimizations and frequencies take significantly longer (5 to 20x typically).



Use efficient methods (e.g. B3LYP DFT) and clusters to model extended systems.



High-K Choices

Dielectric Materials		κ
silicon oxide	SiO_2	3.5
silicon nitride	Si_3N_4	7
aluminum oxide	Al_2O_3	9
zirconium oxide	ZrO_2	25
hafnium oxide	HfO_2	30 - 40

Candidate materials:

ZrO_2 , HfO_2 , and Al_2O_3 are favorable candidates for the gate dielectric

1. Higher dielectric constant than SiO_2
2. Stable with respect to SiO_2 and silicate formation

Challenges:

1. Processing unknown for high-K materials
2. Uniform deposition required
3. Good dielectric properties required (interface states critical)
4. Stoichiometry needs to be controlled
5. Films chemically very stable and difficult to etch
6. Interlayer oxide formation
7. Dopant penetration and crystallization



The ALD Process

Self-terminating Reactions

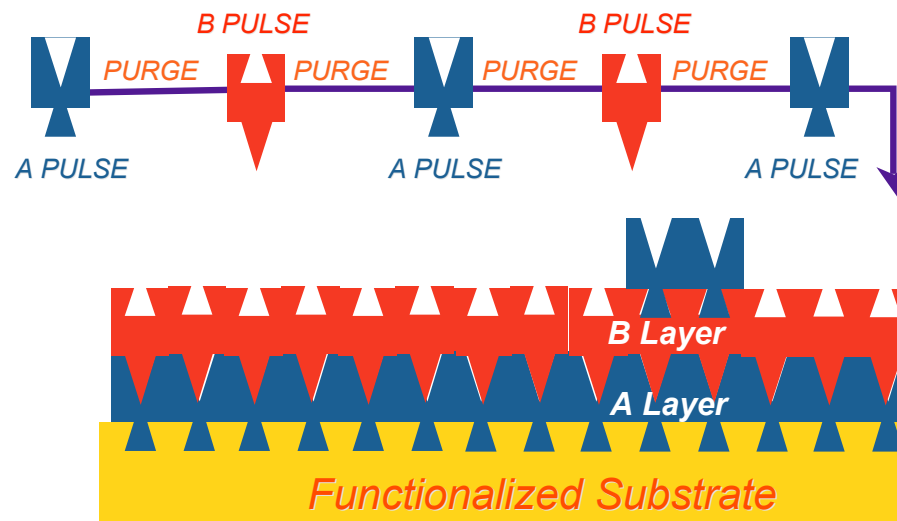
- ALD consists of an alternating sequence of self-terminating **surface** reactions
- Ideally, each step should form a **monolayer**
- Precursors chosen to **not self-react**

Advantages of ALD

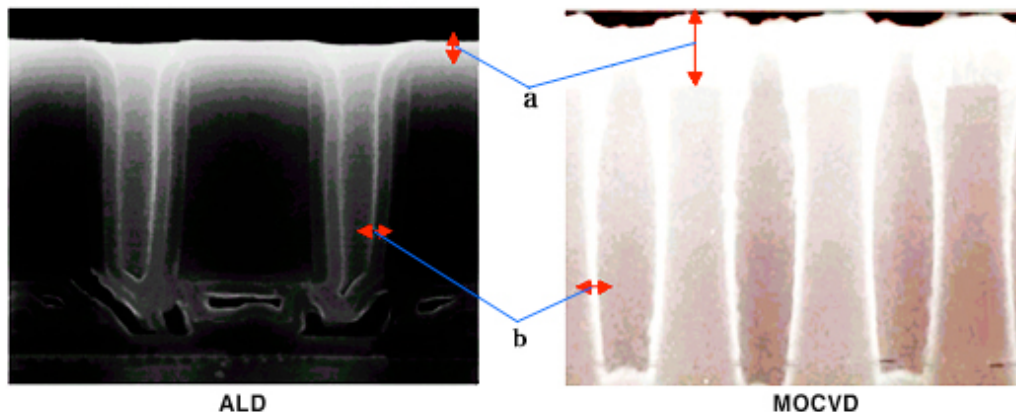
- Excellent **conformality**
- Excellent film **thickness control**
- Excellent **uniformity**
- Excellent control of **stoichiometry**
- **Simpler reactor and process design**

ALD Issues

- Process is slow
- **Submonolayer coverage**
- **Interlayer SiO_2 below ZrO_2 and HfO_2**
- **Contamination**



Adapted from S. George et al.



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

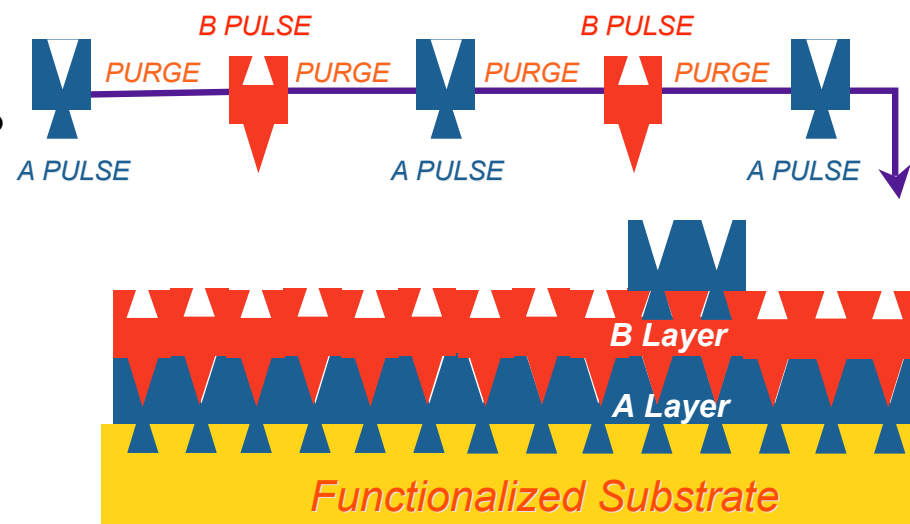
TEM micrographs of Al_2O_3 obtained with ALD and conventional MOCVD process (courtesy of IPS-Tech)



The ALD Process

Questions:

- What are the ALD chemical **mechanisms**?
- What are the optimum ALD process **conditions**?
- How to **select** an ALD precursor?
- How do you **prepare** a surface for ALD?
- What causes **submonolayer** growth?
- What causes **contamination**?
- Can an ALD process be transferred to different **substrates**?
- Can ALD be done **selectively**?



Adapted from S. George.

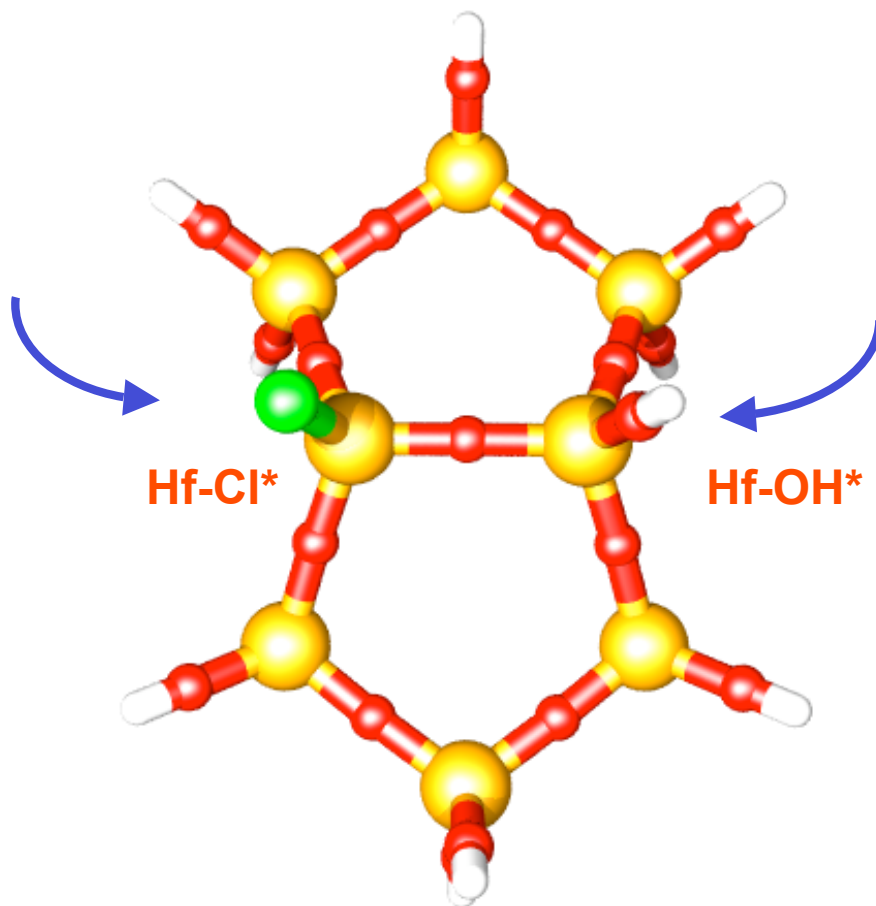
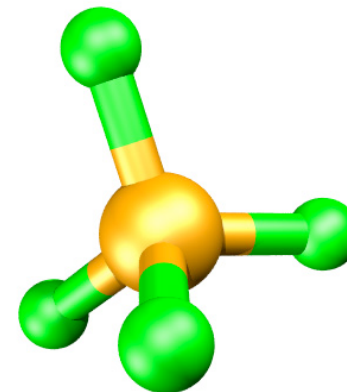


Surface Reaction Models for ZrO_2 and HfO_2 ALD

$H_2O(g)$



$HfCl_4(g)$



$Hf-Cl^*$

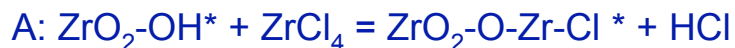
$Hf-OH^*$

HfO_2

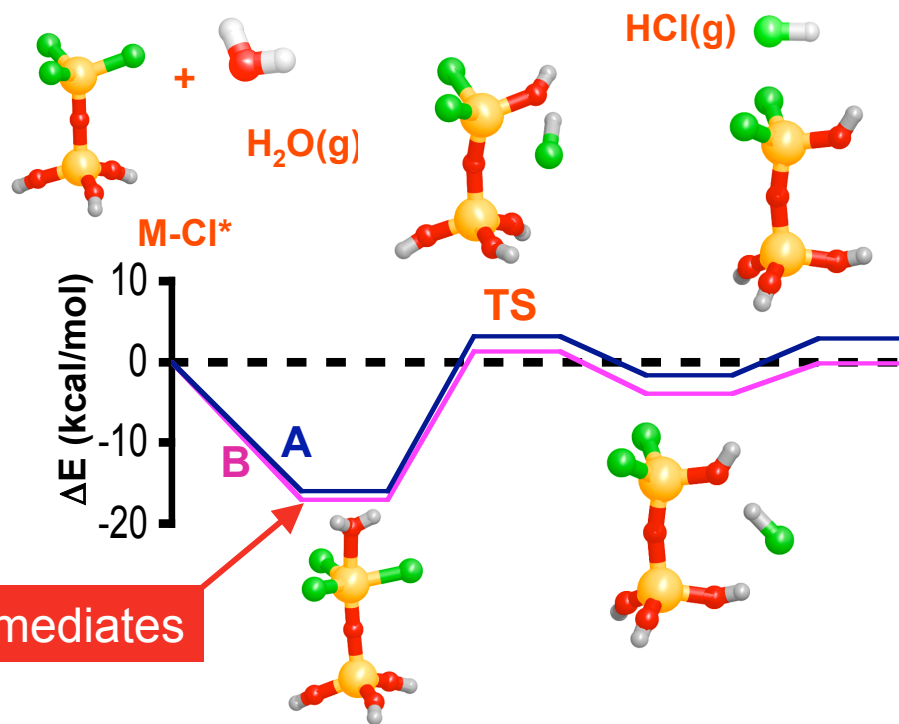
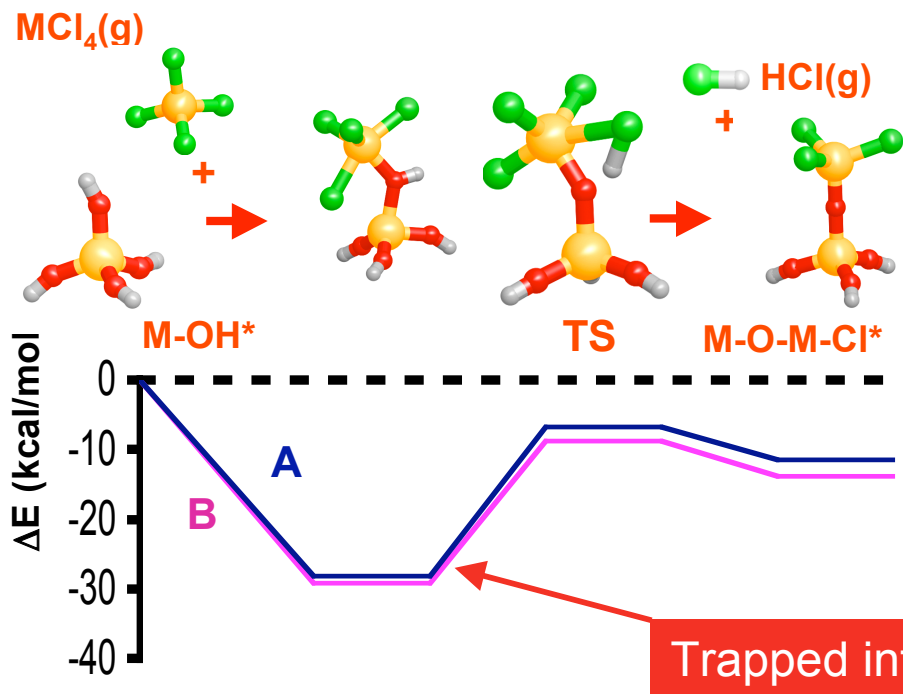
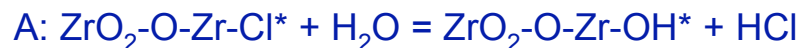


Comparison of ZrO_2 and HfO_2 ALD With MCl_4

MCl_4 Half-Reaction:



H_2O Half-Reaction:

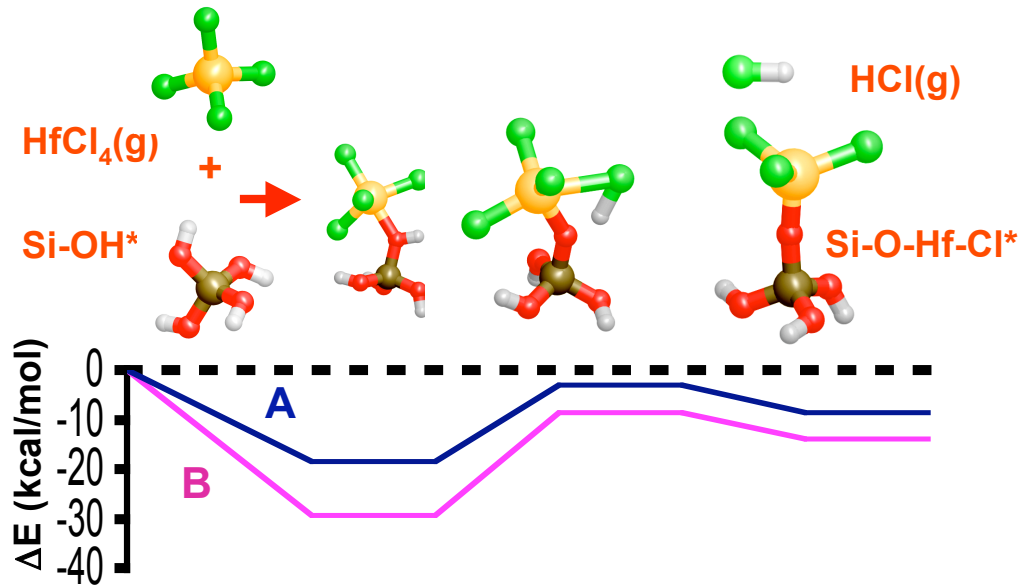
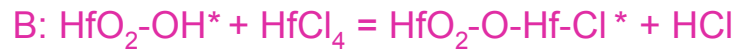
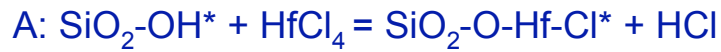


- Chemistry of Zr and Hf is remarkably similar: Ligand exchange reactions
- Precursor desorption predicted for both cases - submonolayer cause?
- Reverse reaction and byproduct readsorption predicted - Cl contamination?
- Relatively high temperatures are required (300-350°C).

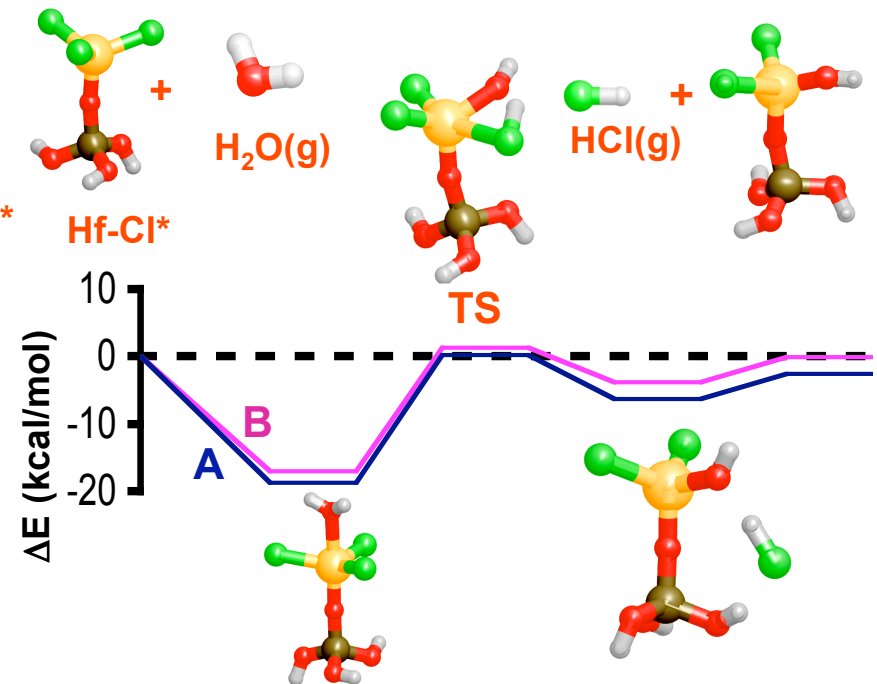
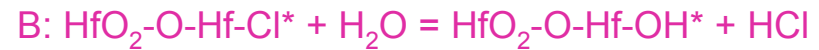
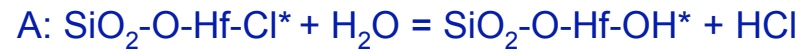


HfO₂ ALD on SiO₂ and HfO₂ Substrates

HfCl₄ Half-Reaction:



H₂O Half-Reaction:



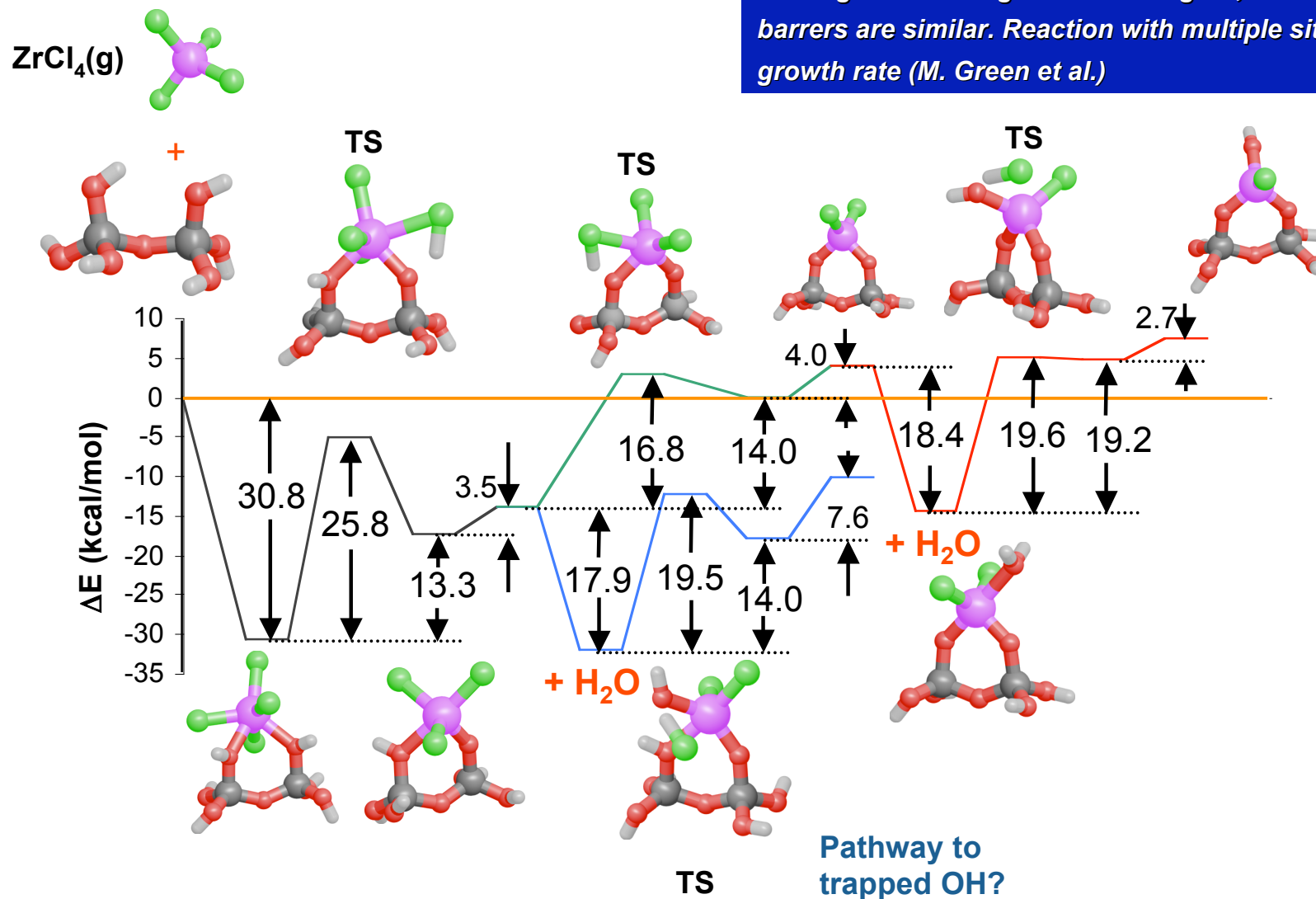
- Substrate only affects kinetics of initial layer if full monolayer growth occurs.
- Temperature determined by barrier relative to trapped intermediate.
- Same issues as with as-grown film.

Han, Gao, Garfunkle, Widjaja, Musgrave, Surf. Sci. (2003).

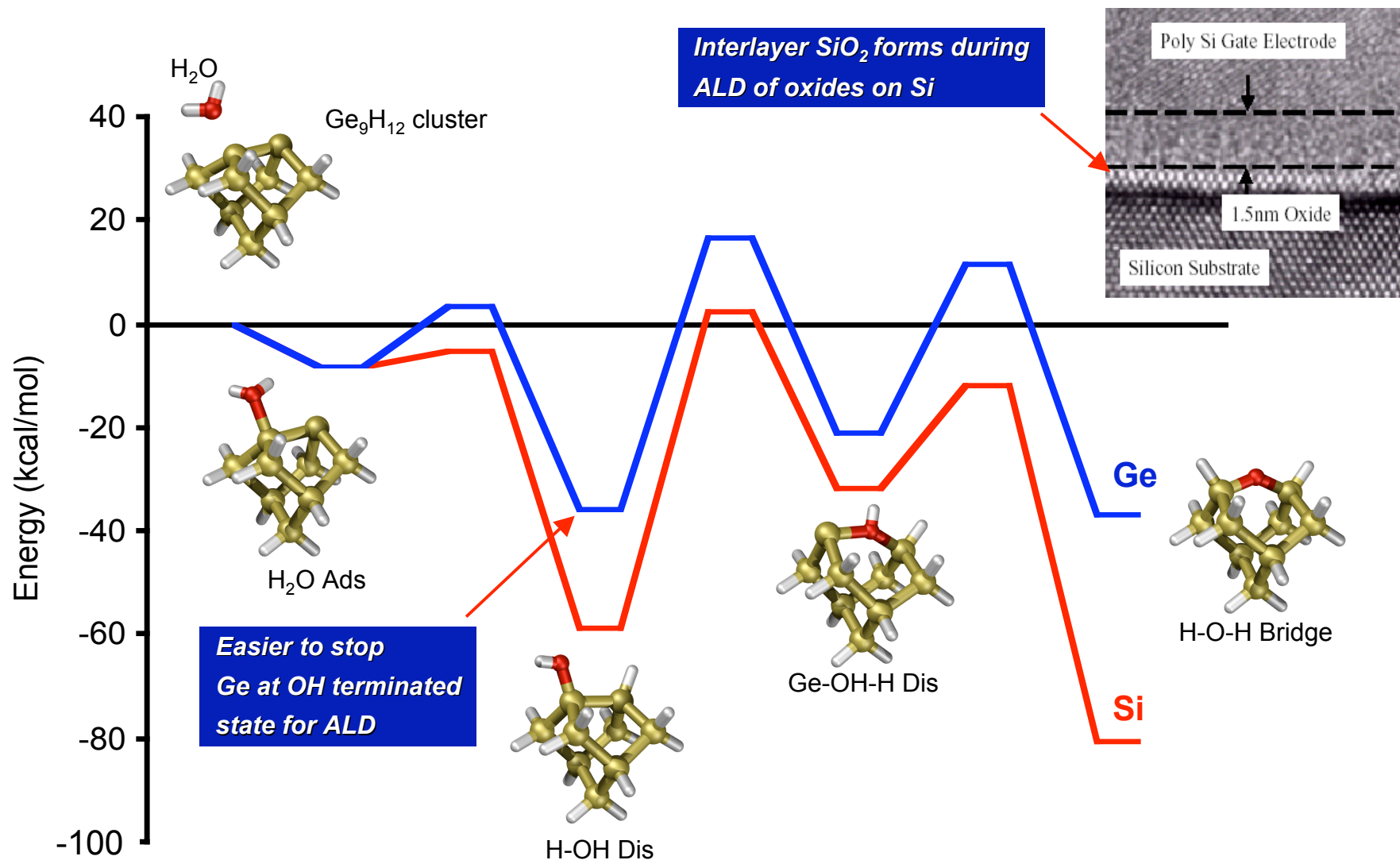


ZrCl₄ ALD Reactions on Multiple OH Sites on SiO₂

First ligand exchange barrier is higher, but subsequent barriers are similar. Reaction with multiple sites lowers growth rate (M. Green et al.)



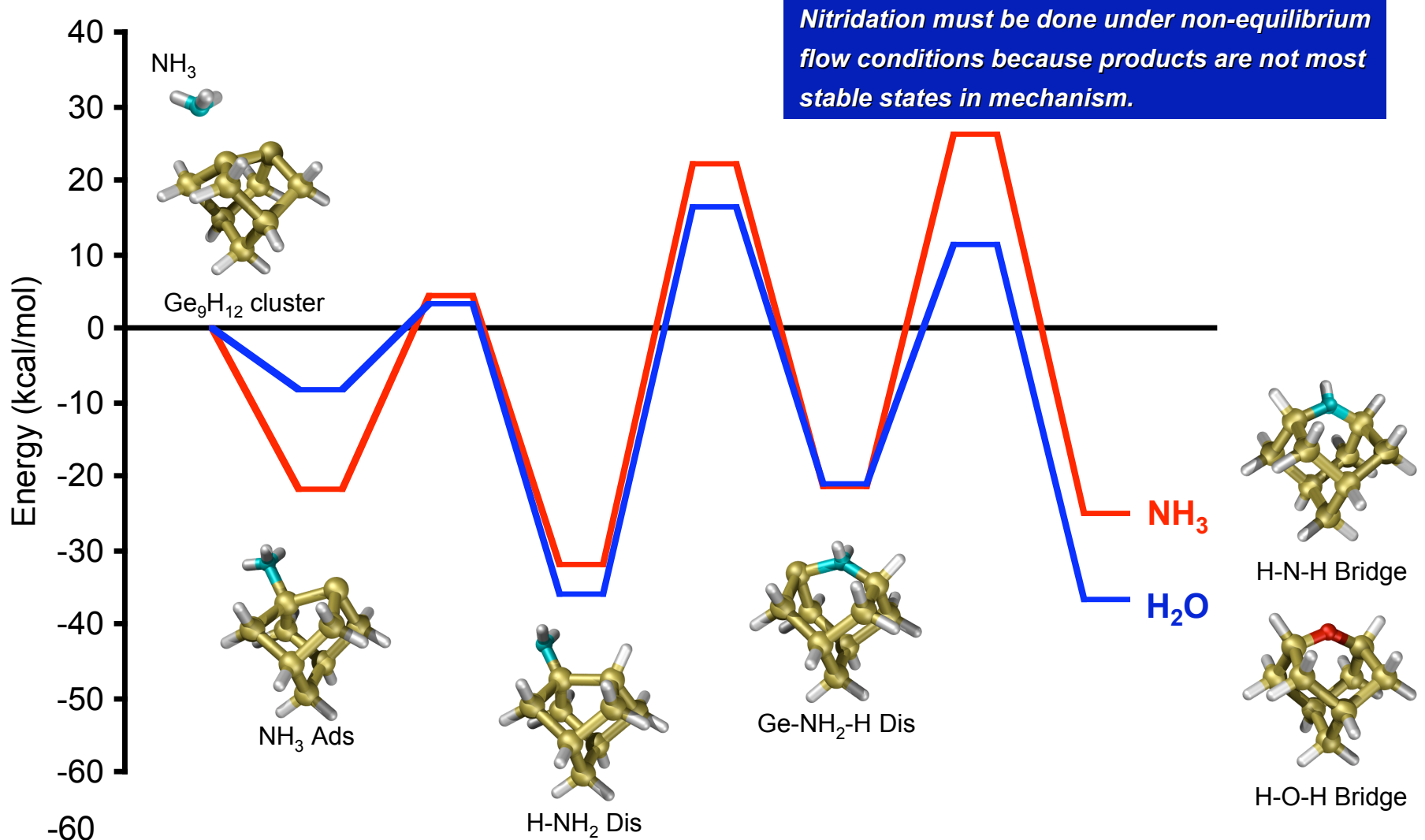
Hydroxylation of Ge(100) with H₂O



Oxide species thermodynamically less stable on the Ge(100) surface



Surface Preparation of Ge: Nitridation with NH_3

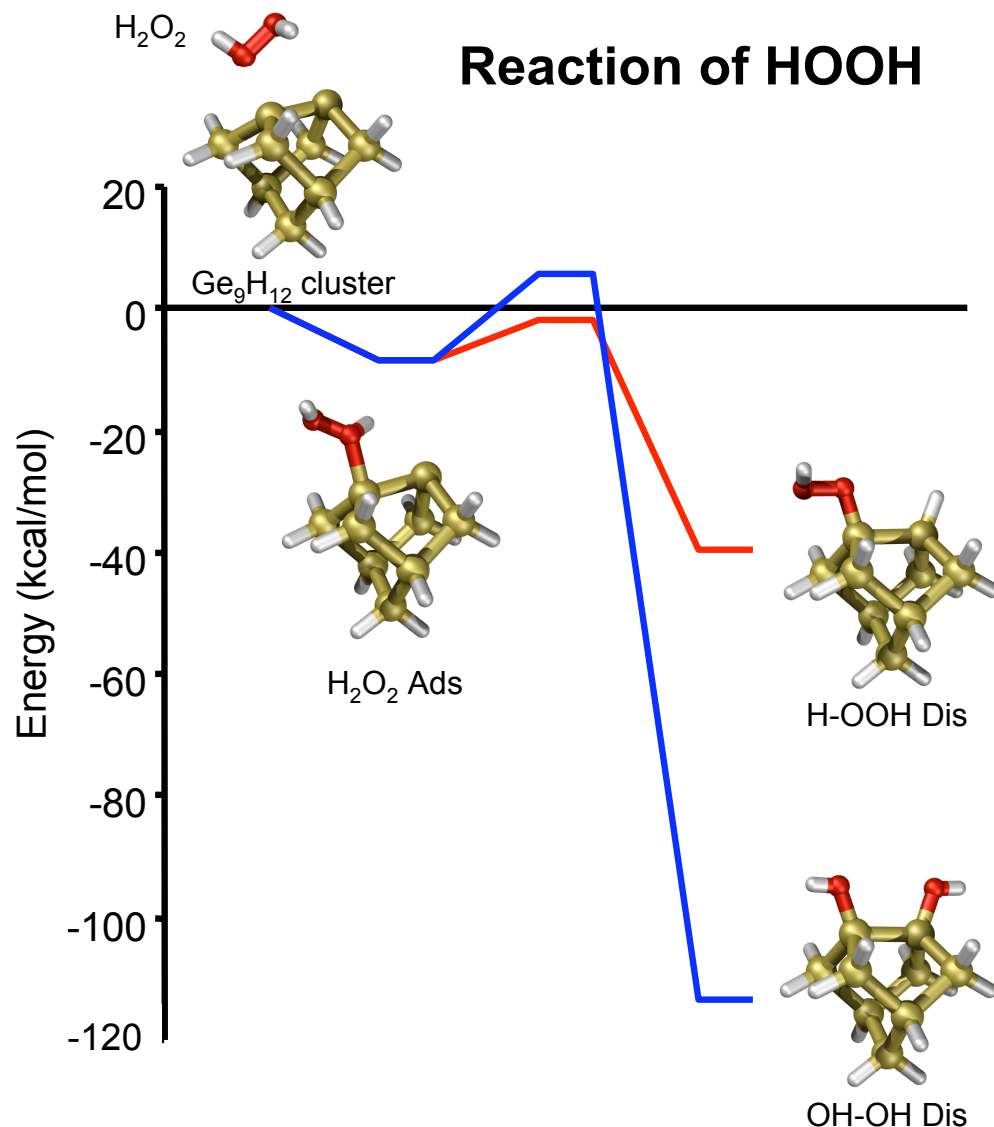


Nitridation involves higher activation barriers.

Mui and Musgrave, J. Phys. Chem. B, Submitted (2004).



Hydroxylation of Ge with H_2O_2

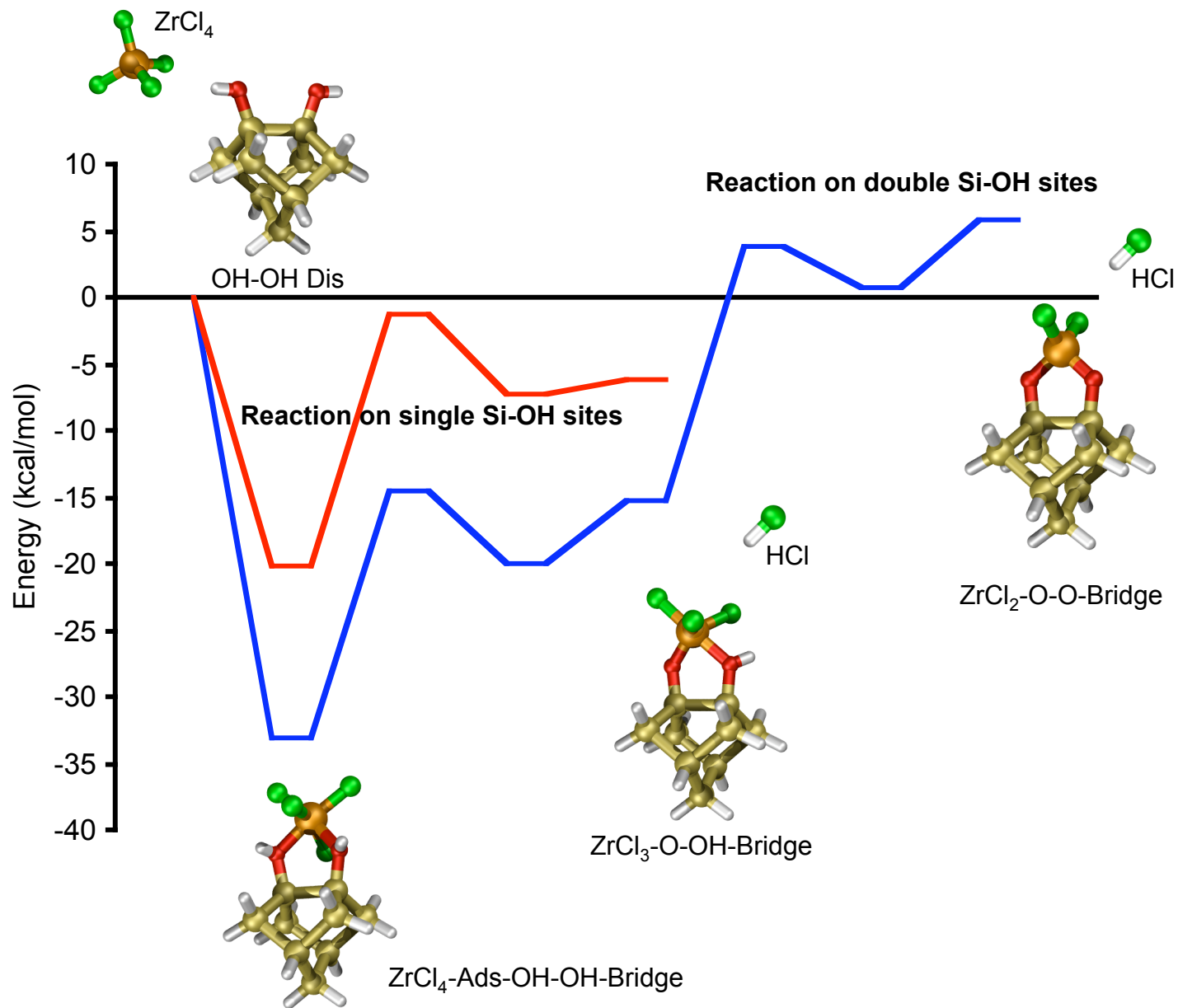


Reactions of HOOH

- Two reaction pathways.
- “OH Dis” pathway generates surface H, and has lower barrier
- “OH-OH Dis” pathway produces two OH groups, which are more stable thermodynamically.
- Also studied further oxidation to bridge-bonded H-O-OH species.



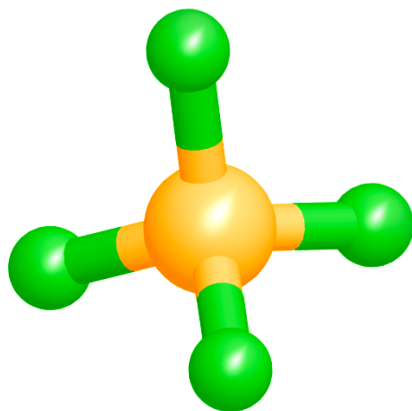
Reaction of $ZrCl_4$ on Hydroxylated Ge



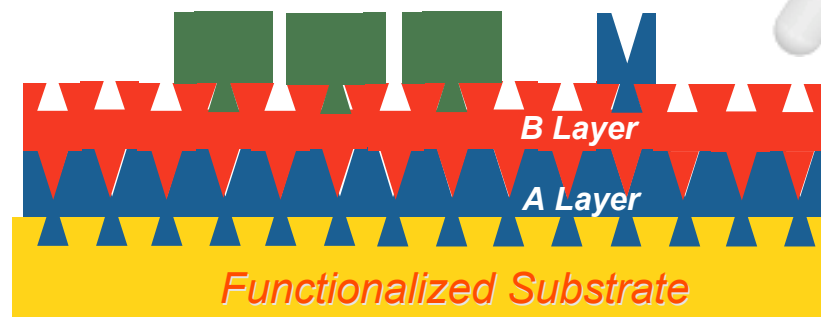
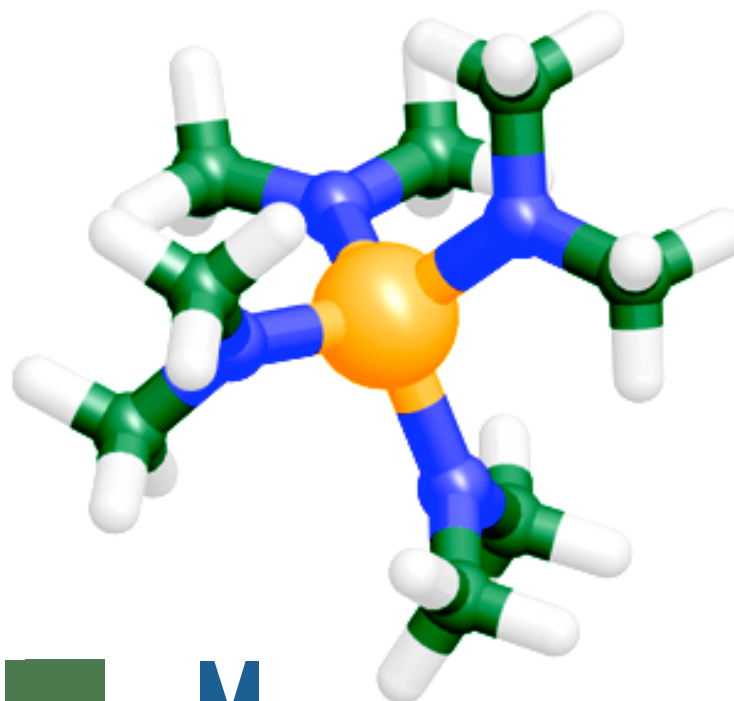
HfO₂ ALD Reactions Using Hf(NMe₂)₄

Will ALD growth rate be slower with Hf(NMe₂)₄ because it is larger than HfCl₄?

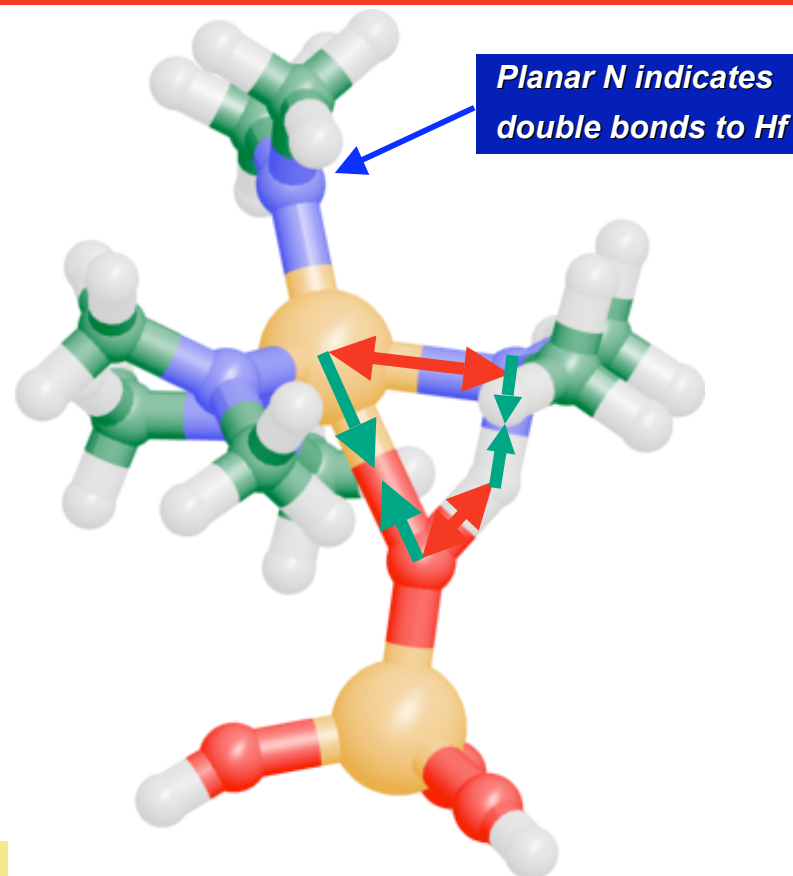
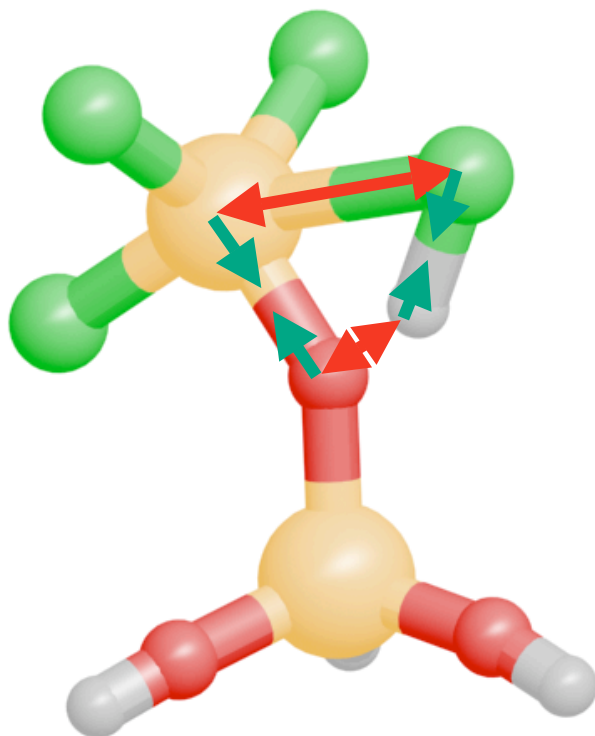
HfCl₄



Hf(NMe₂)₄



Thermochemistry: Relative Bond Strengths



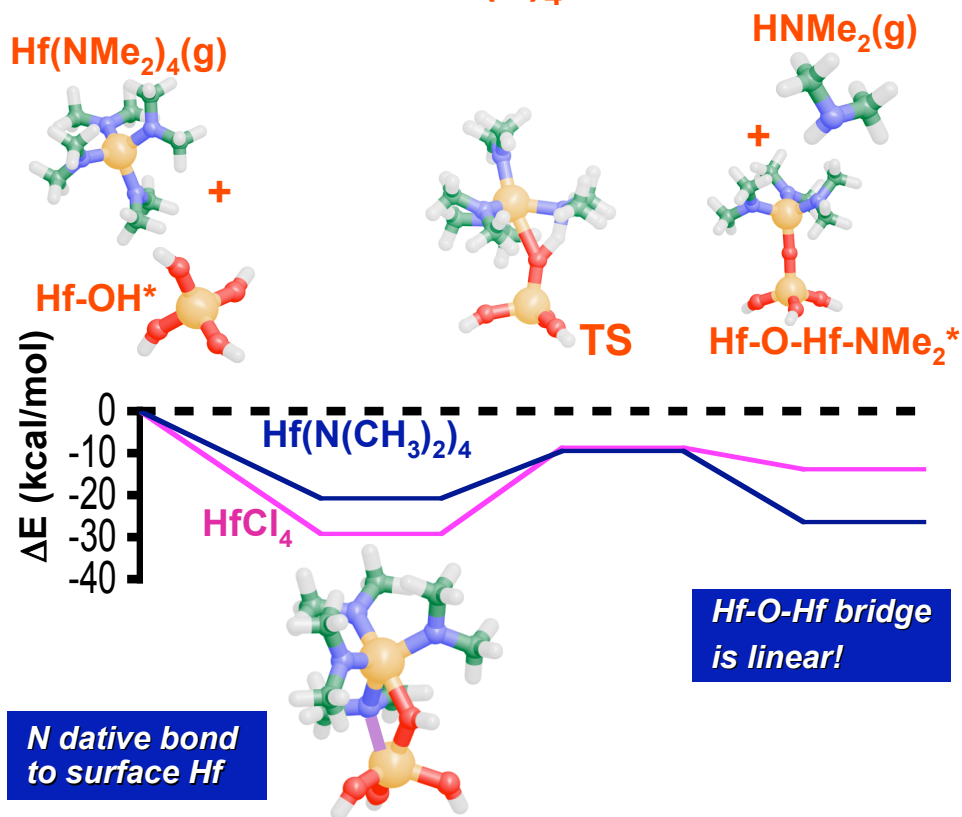
1. Hf-O bond formed and O-H bond broken **in both cases**
2. Broken bond is stronger relative to formed bond in **Metal-chloride** case
3. Formed bond is stronger relative to broken bond in **Metal-alkylamine** case

Bond Energies (kcal/mol)			
	O	Cl	N(CH₃)₂
H-X	114.22	95.04	91.52
Hf-X₄	121.09	103.51	81.03

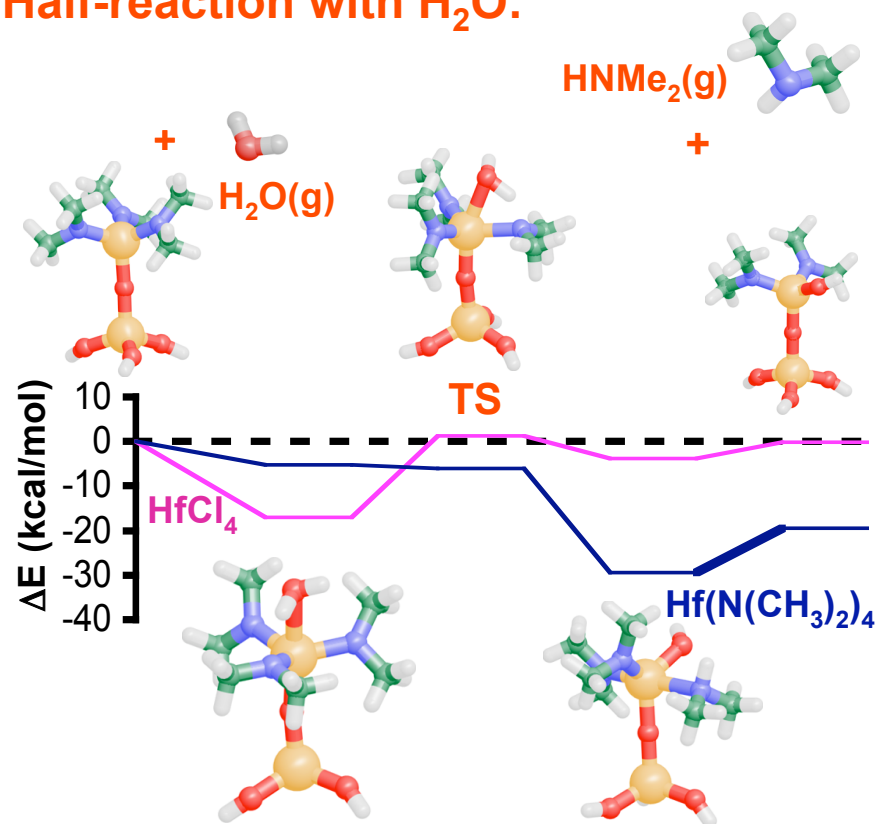


HfO₂ ALD Reactions: Hf(NMe₂)₄ versus HfCl₄

Half-reaction with Hf(X)₄:



Half-reaction with H₂O:



- Hf(N(CH₃)₂)₄ reaction is exothermic and does not exhibit trapping of intermediate state.
- Hf(N(CH₃)₂)₄ barrier is lower: lower ALD temperature.
- Hf(N(CH₃)₂)₄ shown to have higher growth rate than metal chloride process - less precursor desorption and higher surface OH site concentration at reaction temperatures.

Han, Gordon, and Musgrave, Accepted (2004).



1st Half-reaction Non-Growth Ligand Exchange

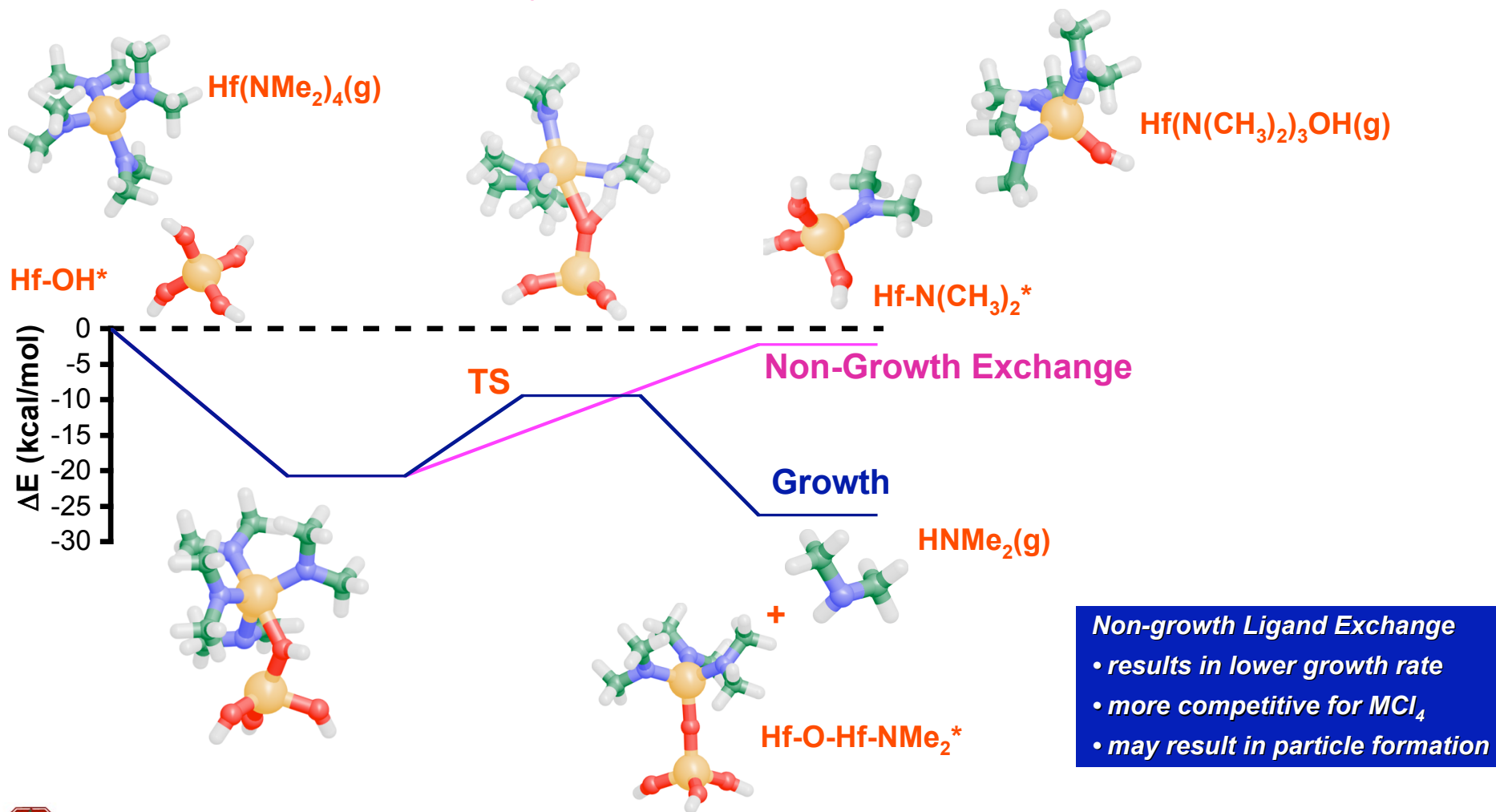
Reaction with Hf(X)₄:



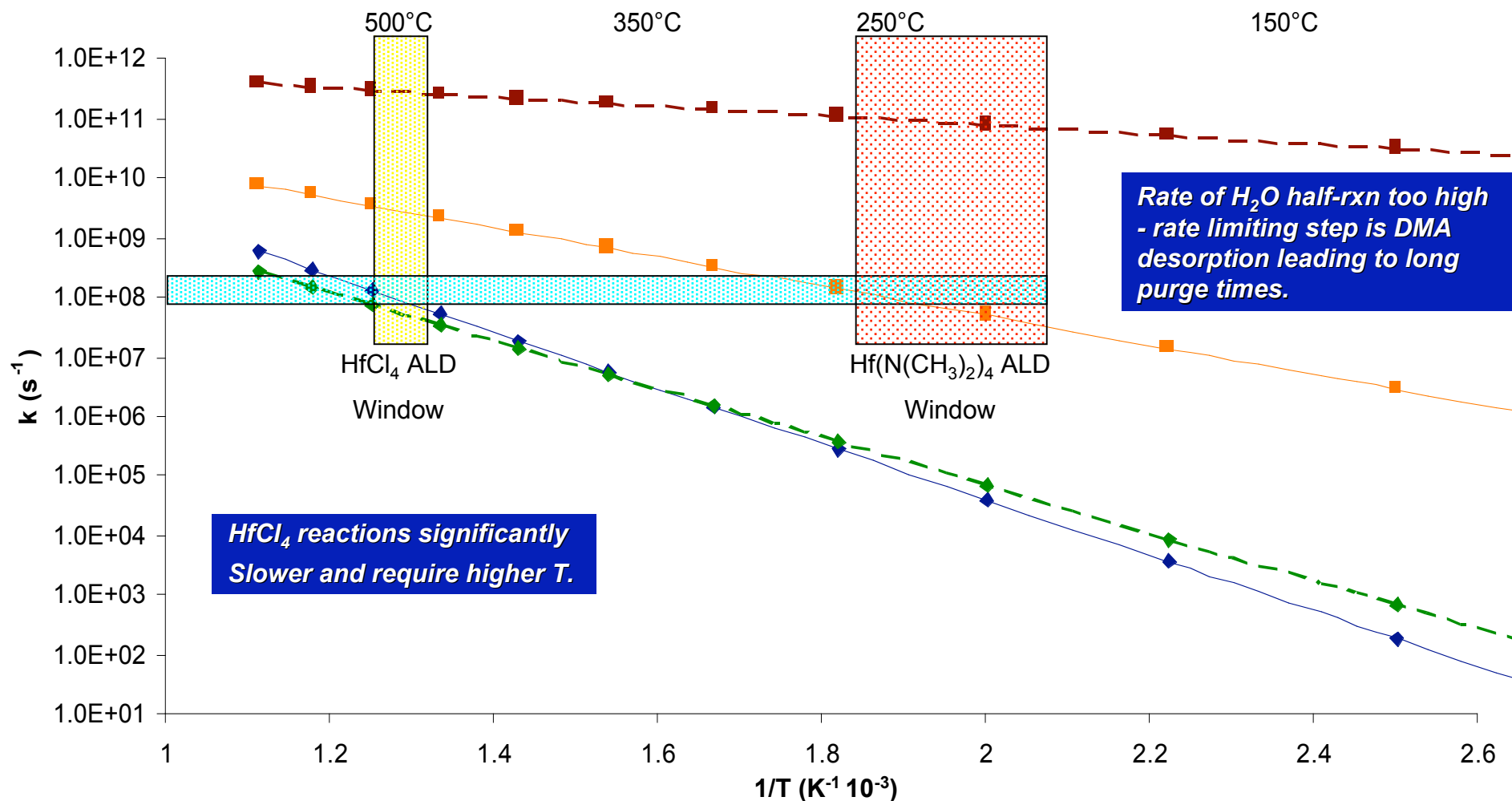
ALD Ligand-Exchange Reaction



Non-Growth Ligand Exchange



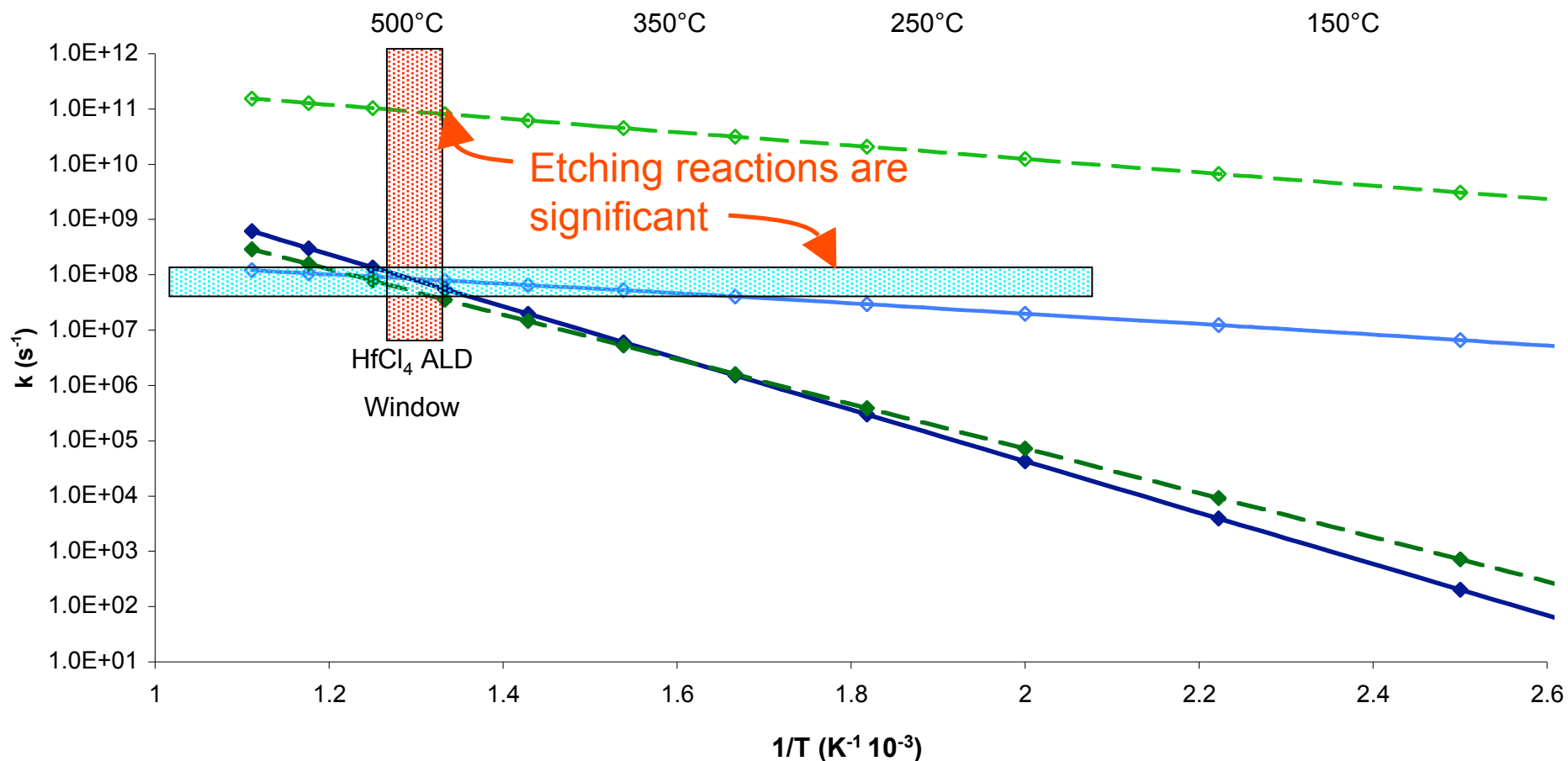
Forward Reaction Rates



		A	n	E _a /R
	HfCl ₄ First Half-Reaction	2.81E+12	0.472	1.05E+04
	HfCl ₄ Second Half-Reaction	3.18E+11	0.450	9.05E+03
	Hf(N(CH ₃) ₂) ₄ First Half-Reaction	4.01E+12	0.017	5.68E+03
	Hf(N(CH ₃) ₂) ₄ Second Half-Reaction	5.72E+11	0.222	1.68E+03



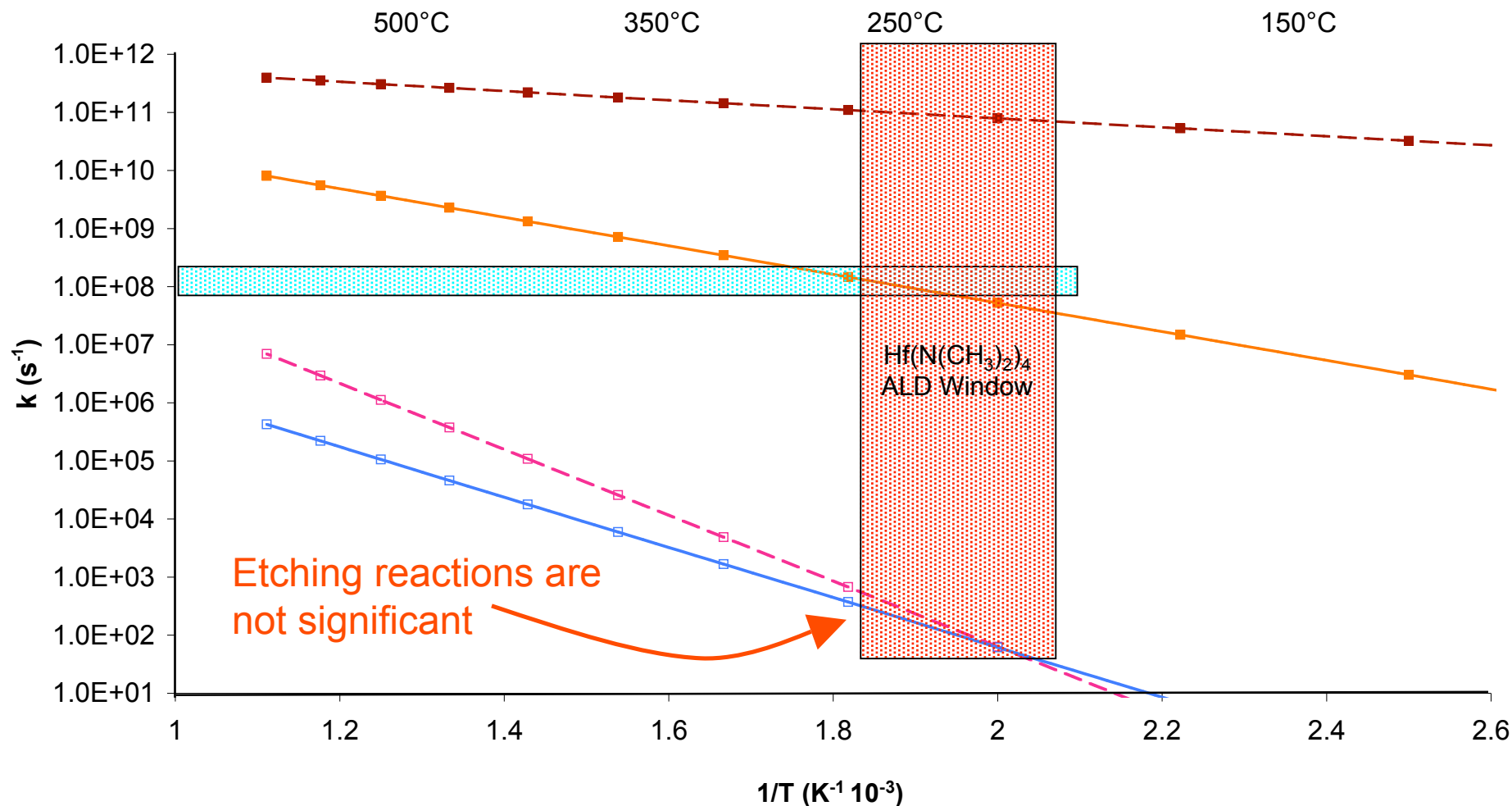
HfCl₄ Forward and Reverse Reaction Competition



		A	n	E _a /R
	HfCl ₄ First Half-Reaction - Forward	2.81E+12	0.472	1.05E+04
	HfCl ₄ Second Half-Reaction - Forward	3.18E+11	0.450	9.05E+03
	HfCl ₄ First Half-Reaction - Reverse	1.51E+10	-0.321	2.34E+03
	HfCl ₄ Second Half-Reaction - Reverse	7.90E+11	0.197	2.69E+03



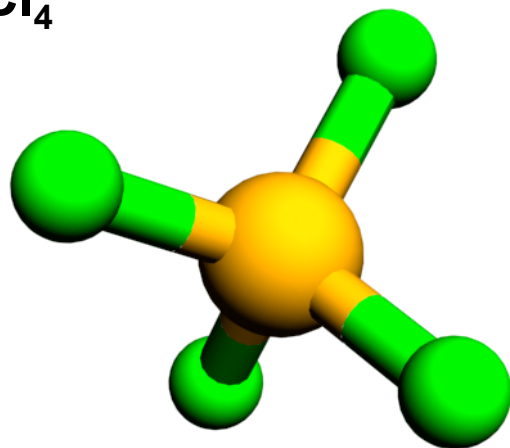
Hf(N(CH₃)₂)₄ Forward and Reverse Reaction Competition



		A	n	E _a /R
	Hf(N(CH ₃) ₂) ₄ First Half-Reaction - Forward	4.01E+12	0.017	5.68E+03
	Hf(N(CH ₃) ₂) ₄ Second Half-Reaction - Forward	5.72E+11	0.222	1.68E+03
	Hf(N(CH ₃) ₂) ₄ First Half-Reaction - Reverse	2.01E+09	0.344	9.72E+03
	Hf(N(CH ₃) ₂) ₄ Second Half-Reaction - Reverse	1.08E+12	0.341	1.28E+04

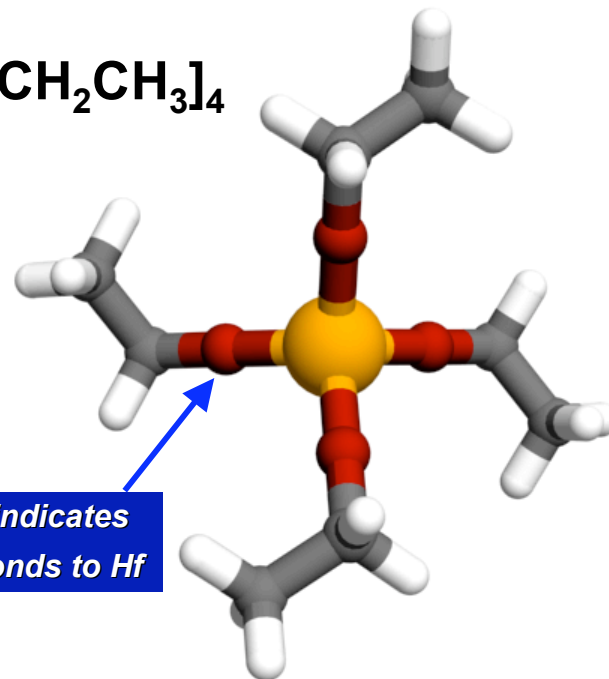


Alkoxides as Alternative ALD Precursor



Metal Chlorides

- Commonly used
- Simple structure
- HCl by-product
- Precursor desorption
- High deposition temperatures

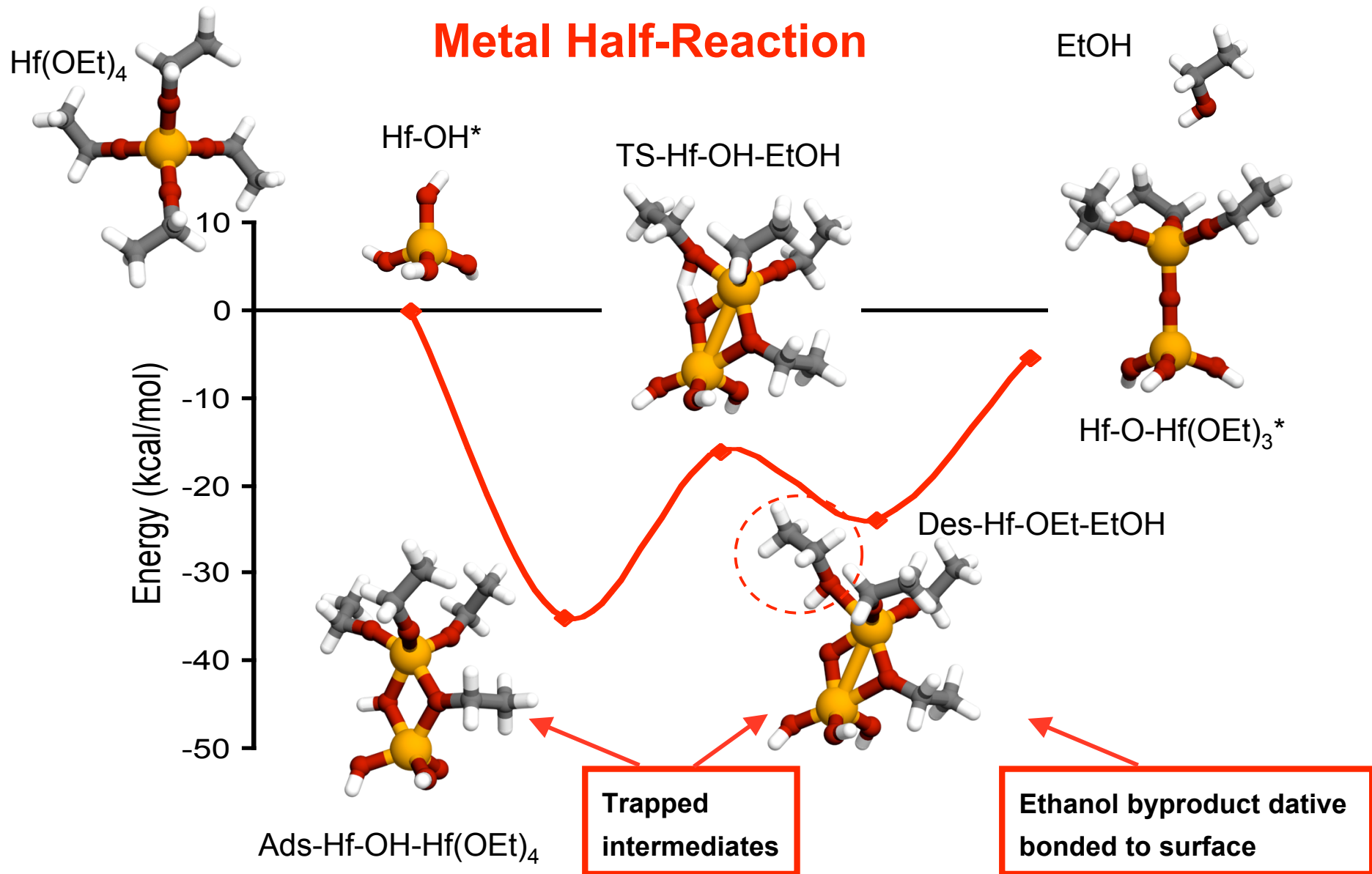


Metal Alkoxide

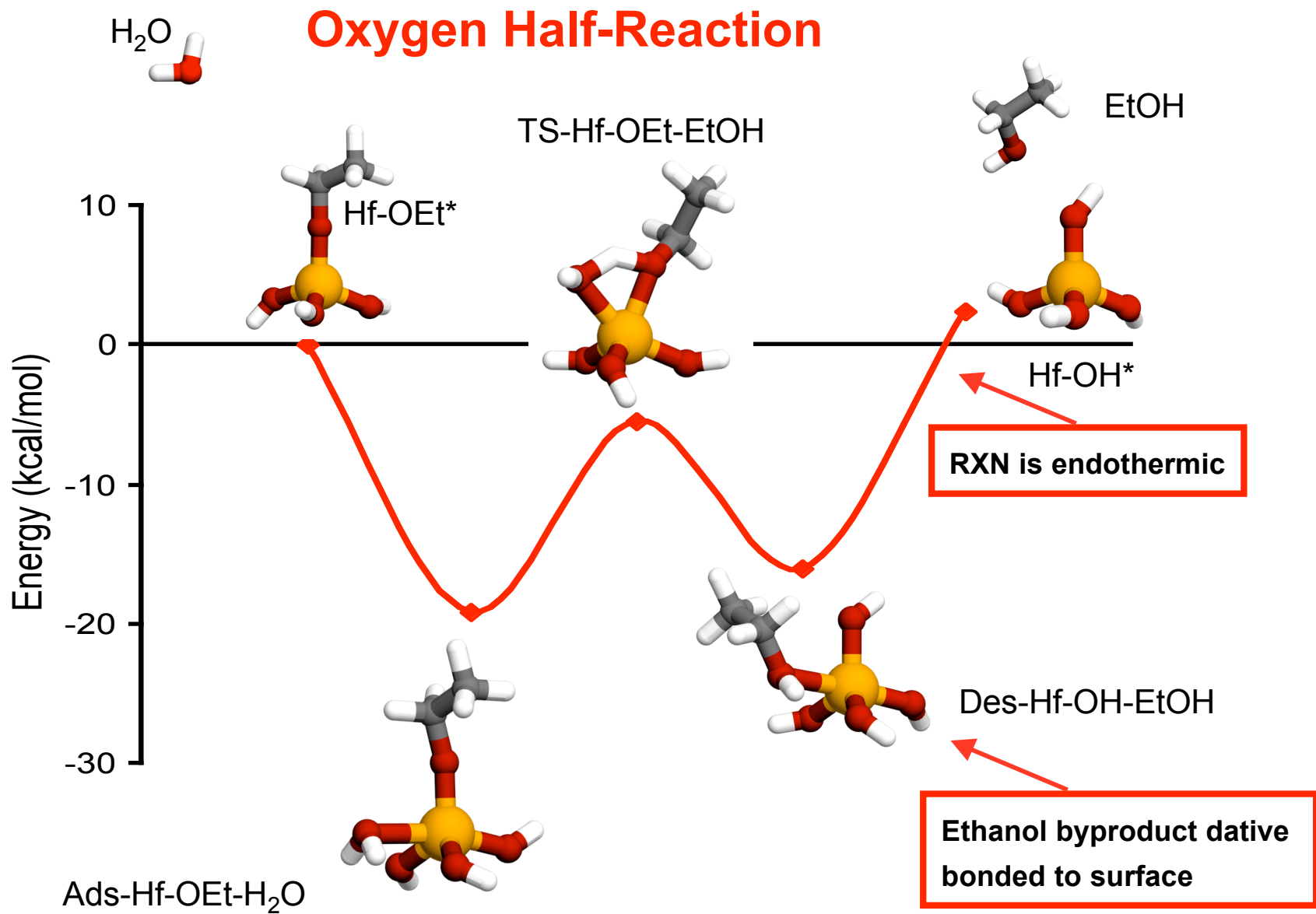
- Metal and oxygen precursor
- Organic by-product.
- Possibility of mixed thin films.
- Reactivity can be tuned.



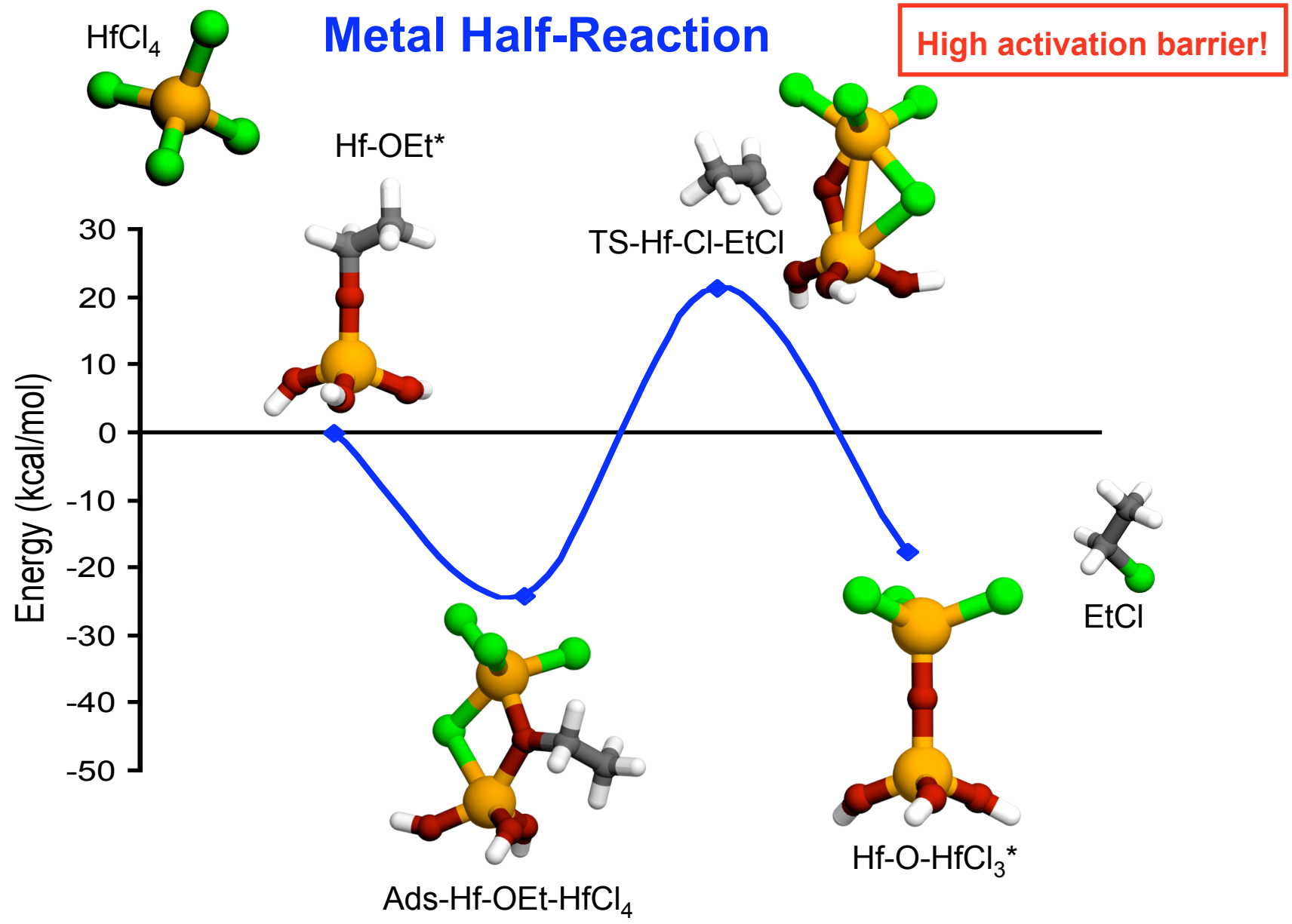
ALD of HfO_2 with $\text{Hf}(\text{OEt})_4$ and H_2O



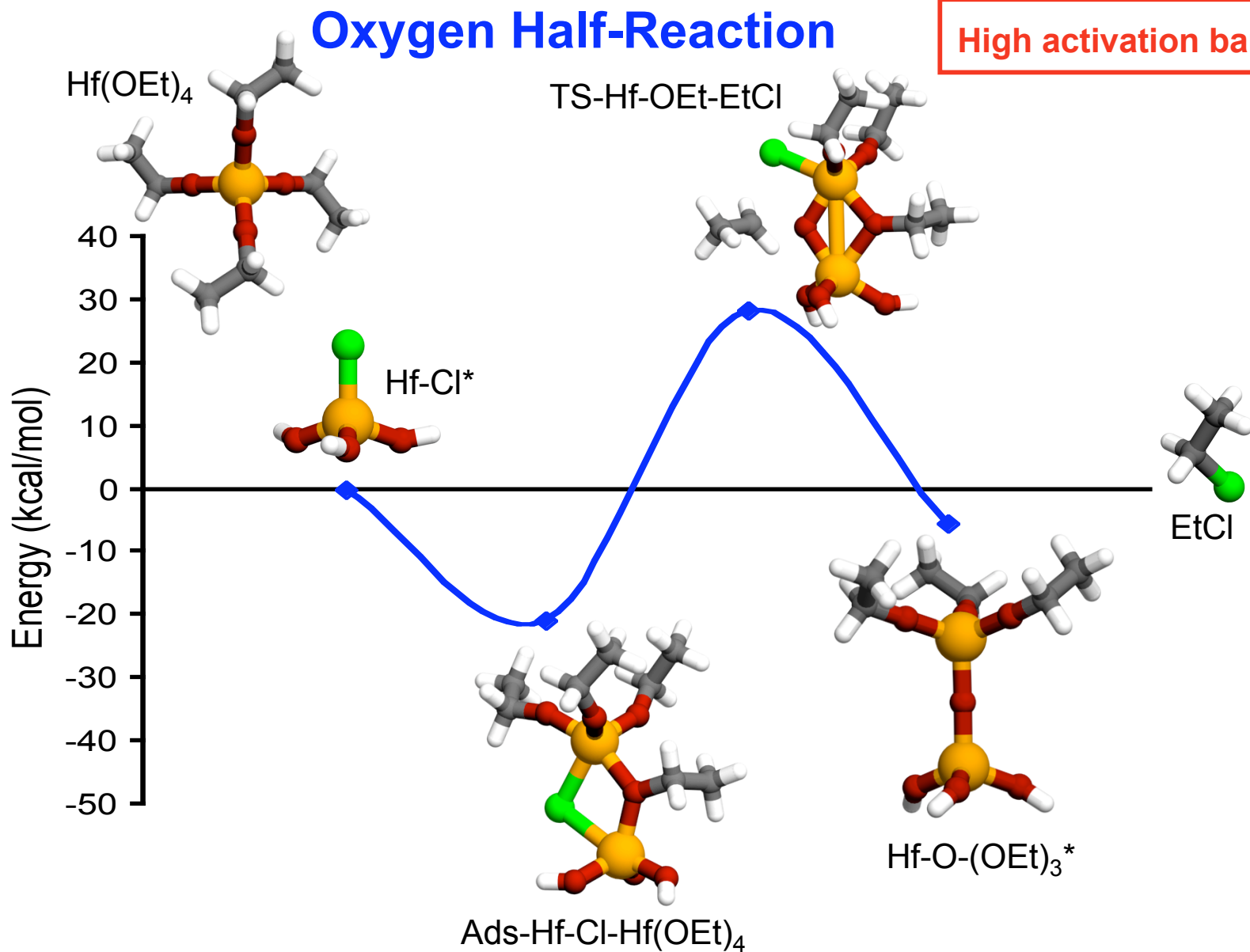
ALD of HfO_2 with $\text{Hf}(\text{OEt})_4$ and H_2O



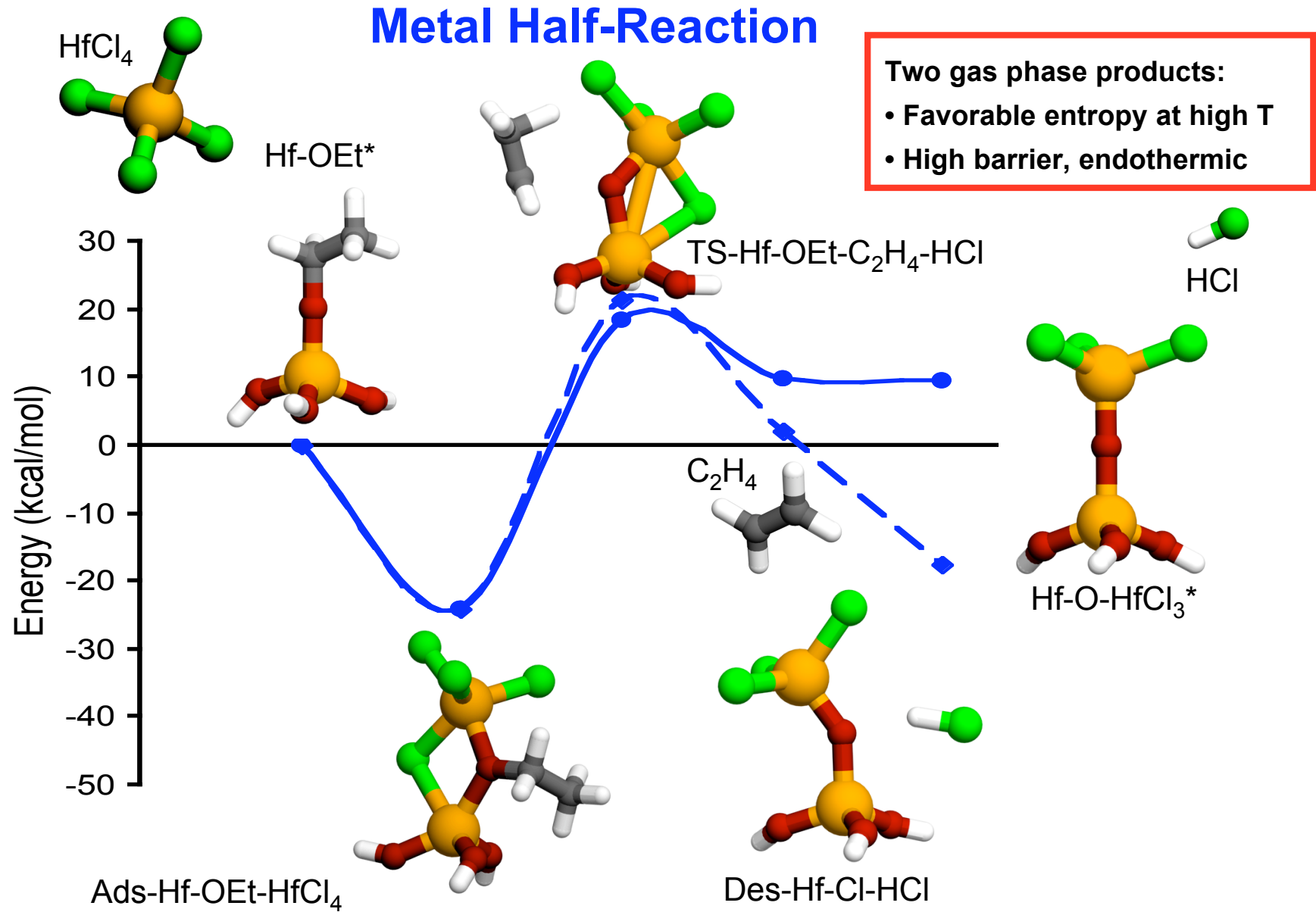
ALD with HfCl_4 and $\text{Hf}(\text{OEt})_4$ as Oxygen Source



ALD with HfCl_4 and $\text{Hf}(\text{OEt})_4$ as Oxygen Source

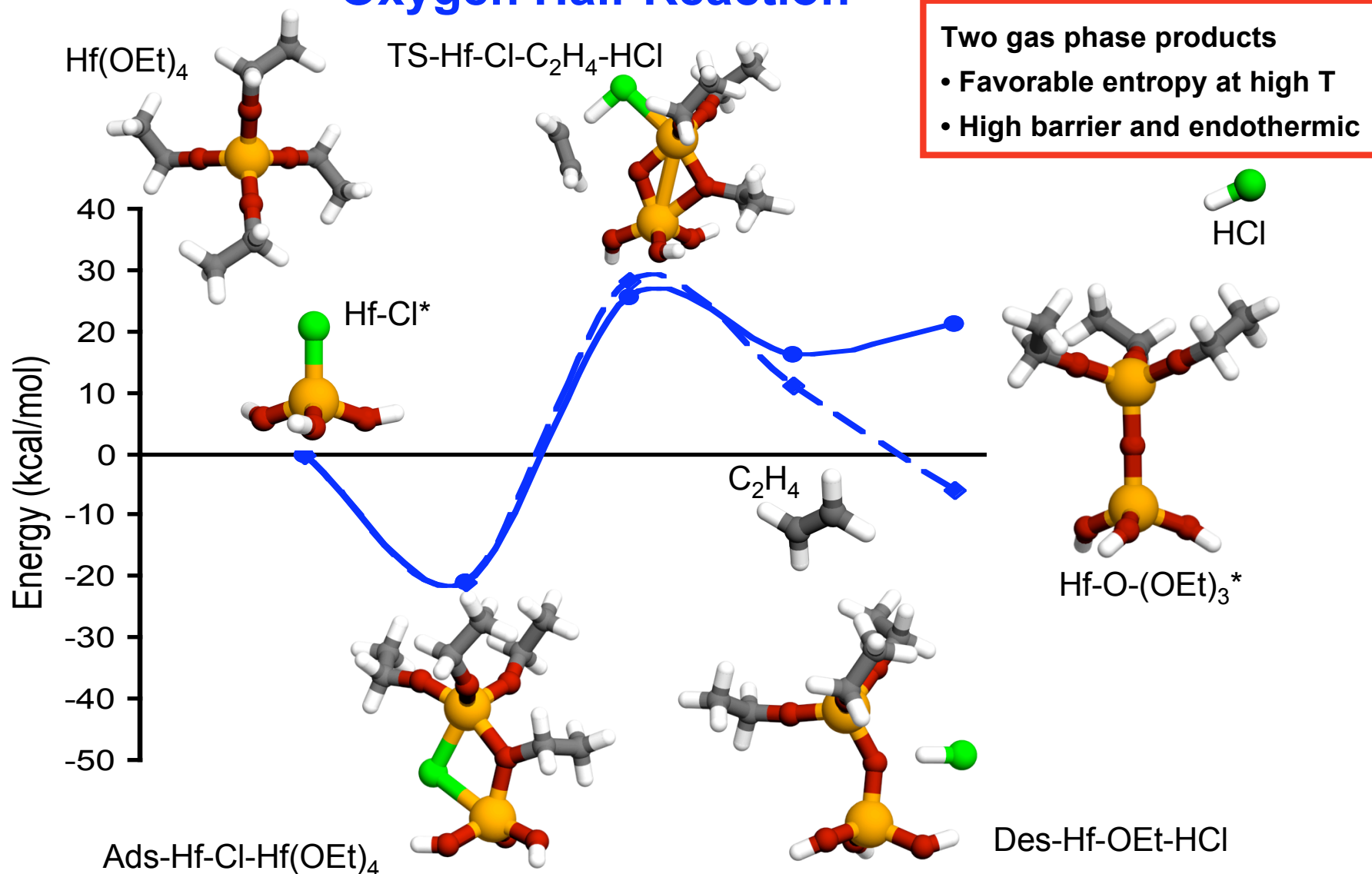


Alternative Mechanism



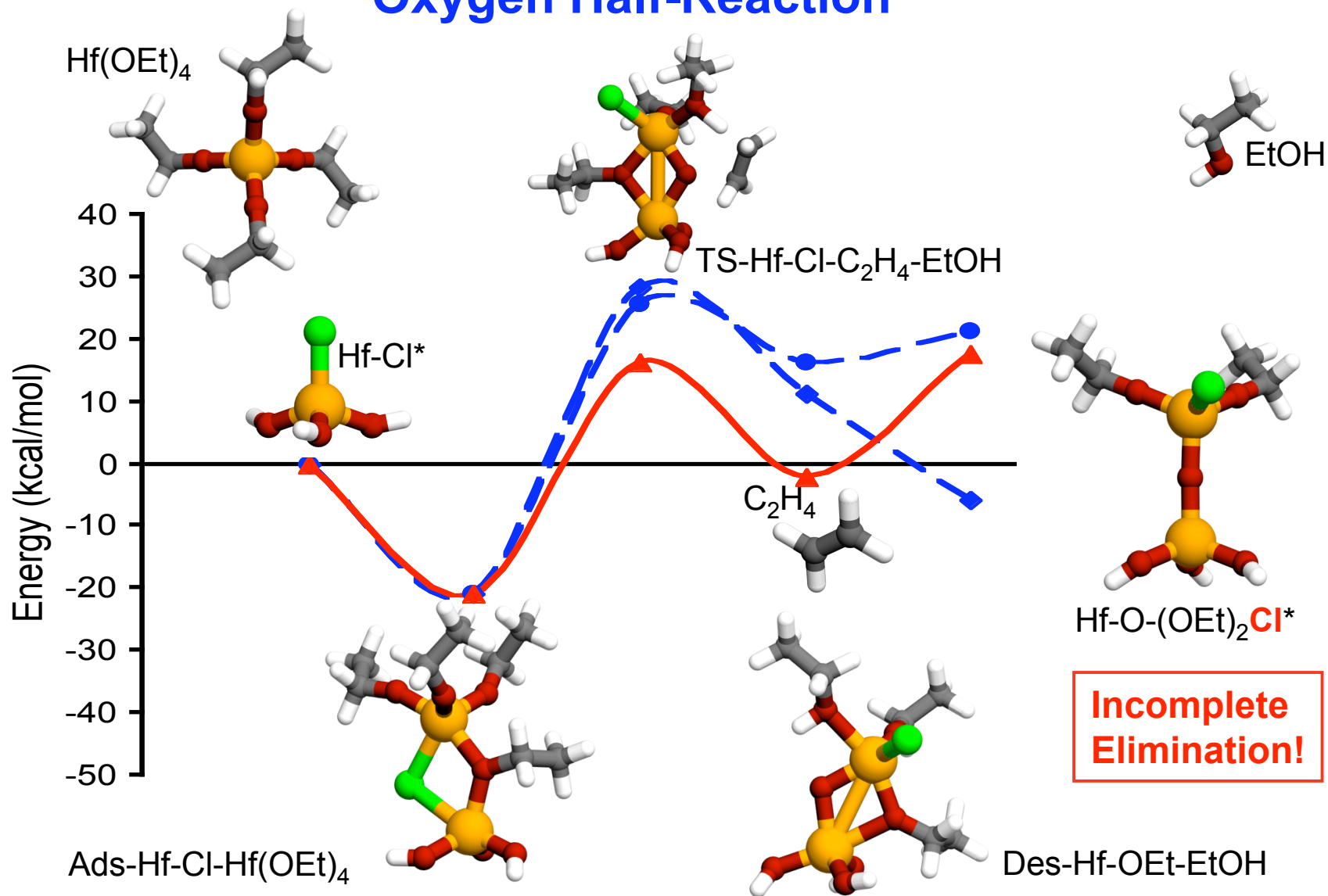
Alternative Mechanism for EtCl Elimination

Oxygen Half-Reaction



Incomplete Cl Elimination

Oxygen Half-Reaction



Metal Oxide ALD Precursor Selection

Metal chlorides:

- Require high temperatures
- Almost thermalneutral
- Lead to trapped intermediates
- Readsorption of HCl-etching and corrosion
- Cl contamination
- Competitive non-growth ligand exchange reactions

Alkylamides:

- Require lower temperatures
- Less strongly trapped intermediates
- Thermodynamic driving force
- Less competition with non-growth ligand exchange reactions

Alkoxides:

- Require higher temperatures
- Two strongly trapped intermediates and strongly bound by-products
- Little thermodynamic driving force
- Various competitive reactions
- Very expensive oxygen source
- Various contamination pathways



ALD on Organics

AS-ALD Motivation

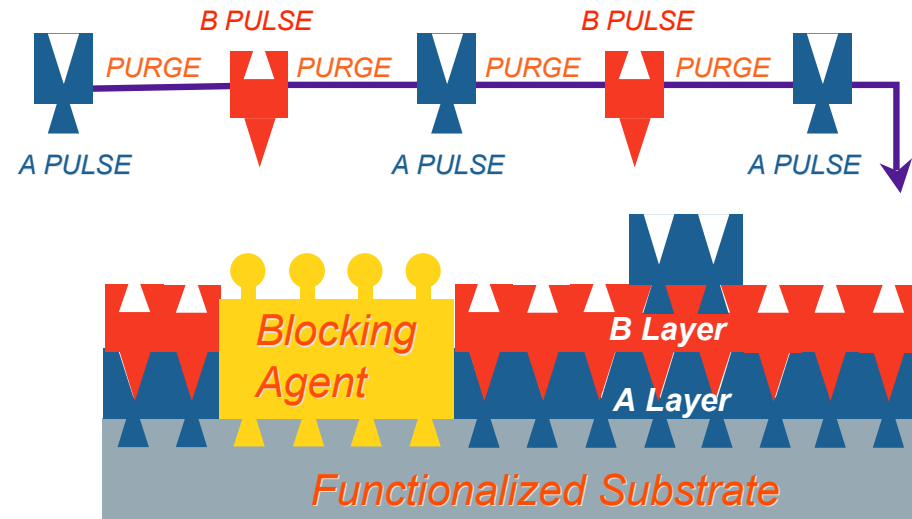
- Etching of HfO_2 and ZrO_2 is difficult.
- High-K etch may require specialized masks.

Area Selective ALD

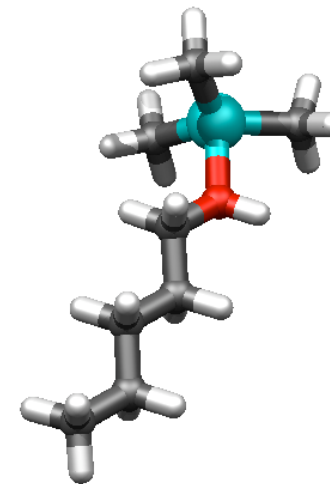
- AS-ALD requires patterning the surface with an agent which inhibits ALD.
- Masking agent must not thermally decompose at ALD temperature.
- Masking agent must lead to highly selective ALD growth.
- ALD precursors should be chosen which react at low temperatures.
- ALD precursors must have fast kinetics and high growth rates to reduce the number of ALD cycles the masking agent must be exposed to.

ALD for Contact to Molecular Devices

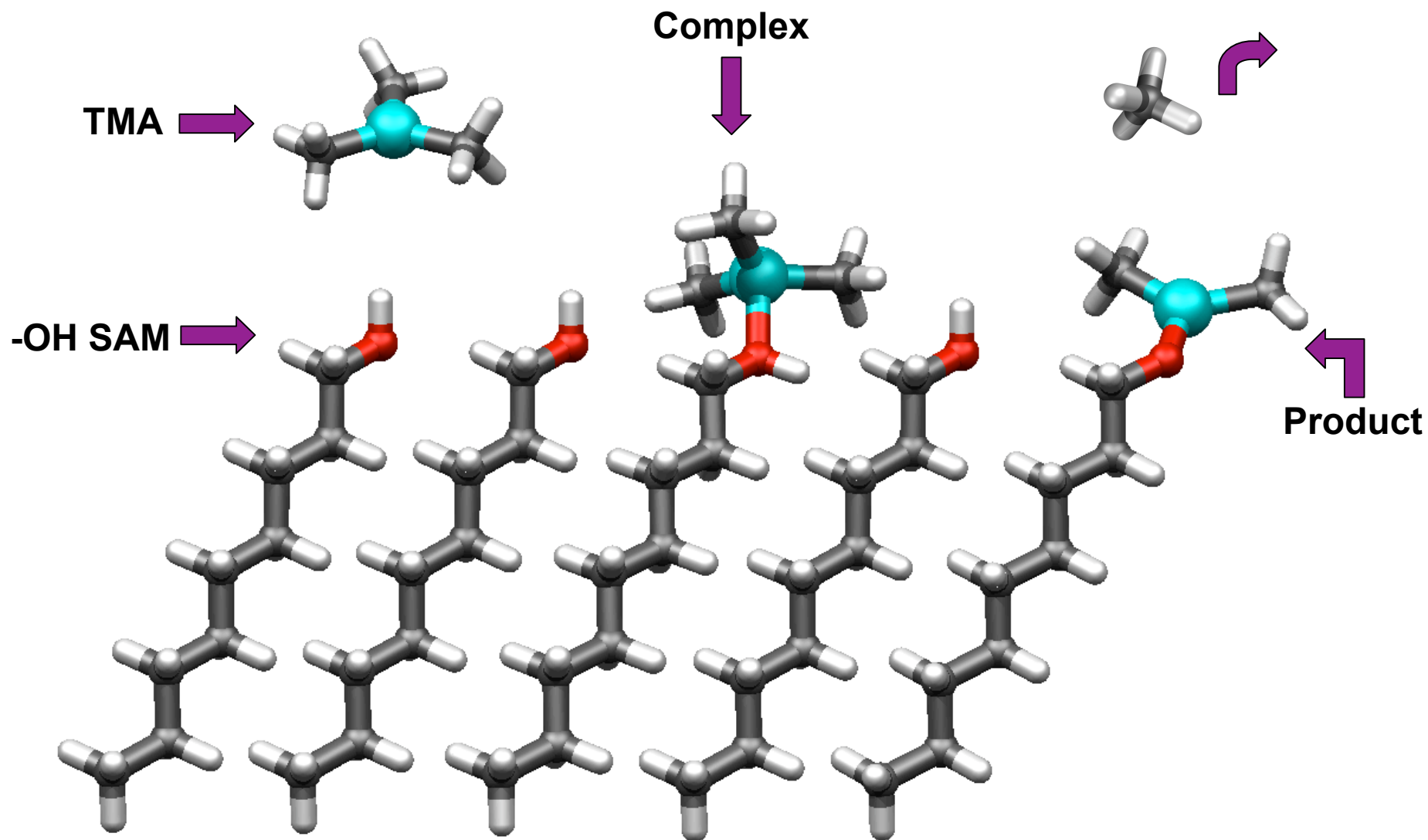
- Choose molecular functionalization to initiate ALD
- Gentle metallization
- Controlled contact formation
- Molecule left intact.



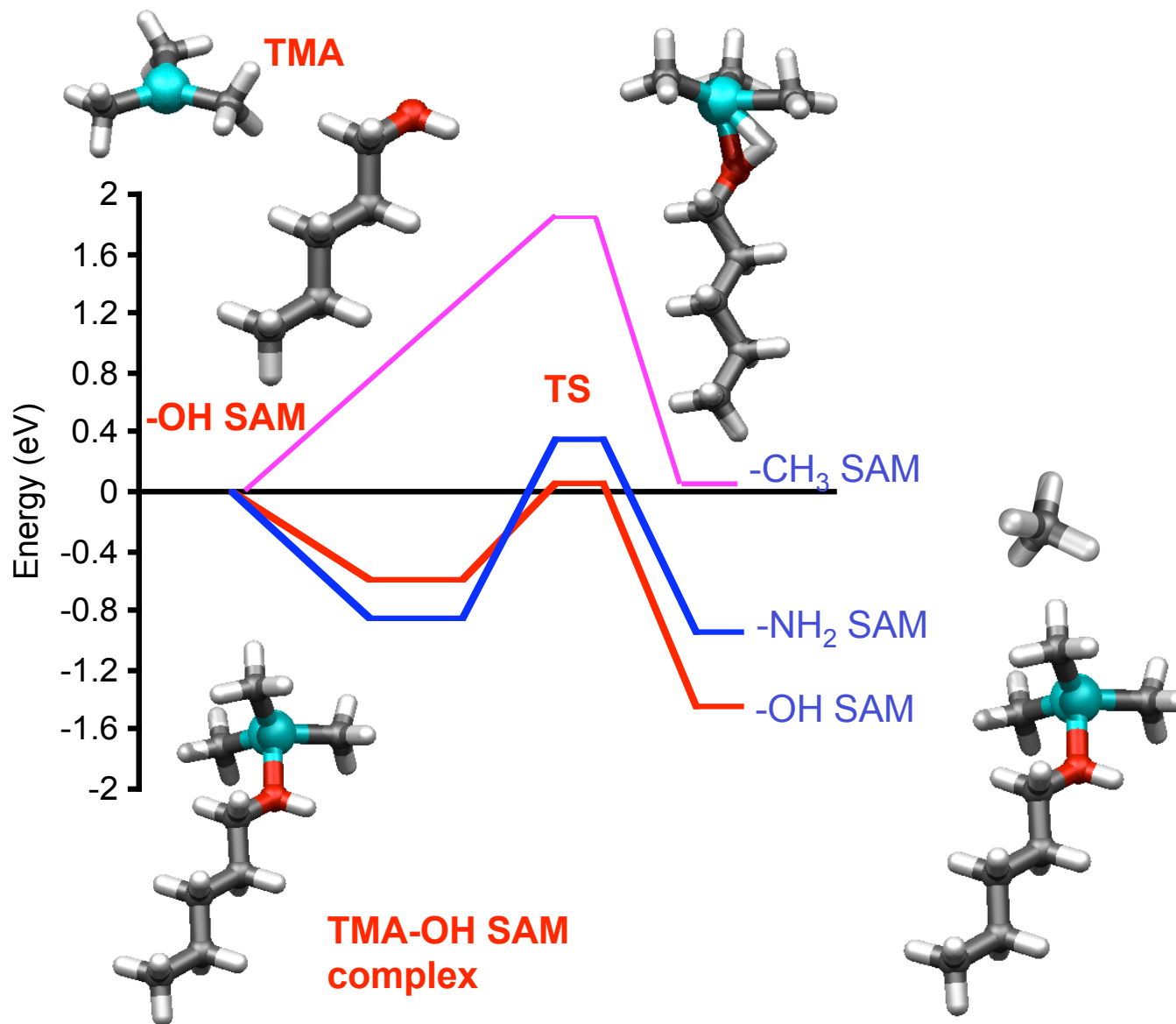
With Bent, and McIntyre



Reaction between TMA and SAMs



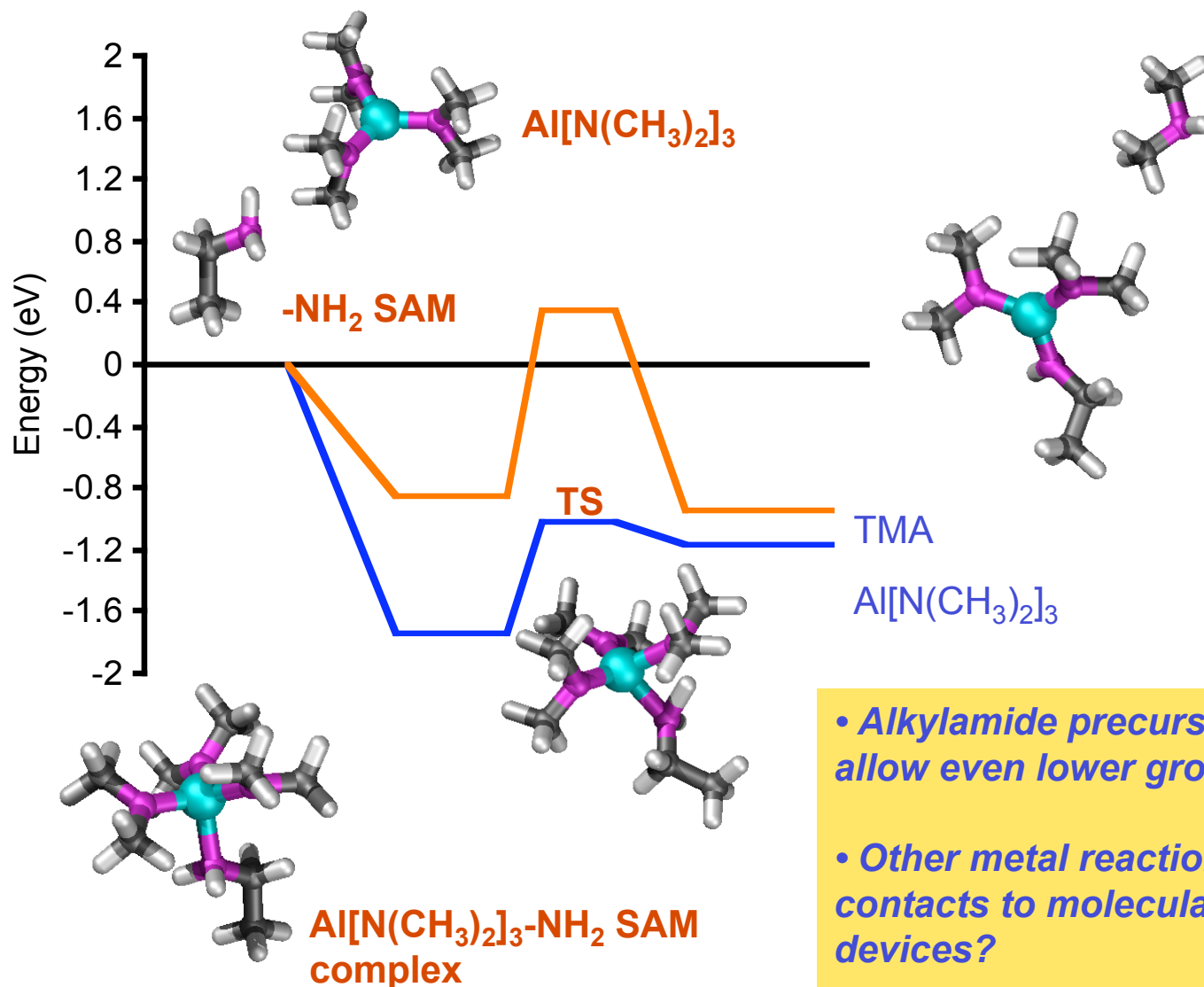
Reaction Barrier for TMA on SAMs



Xu and Musgrave, In press, Chem. Mat. (2004).



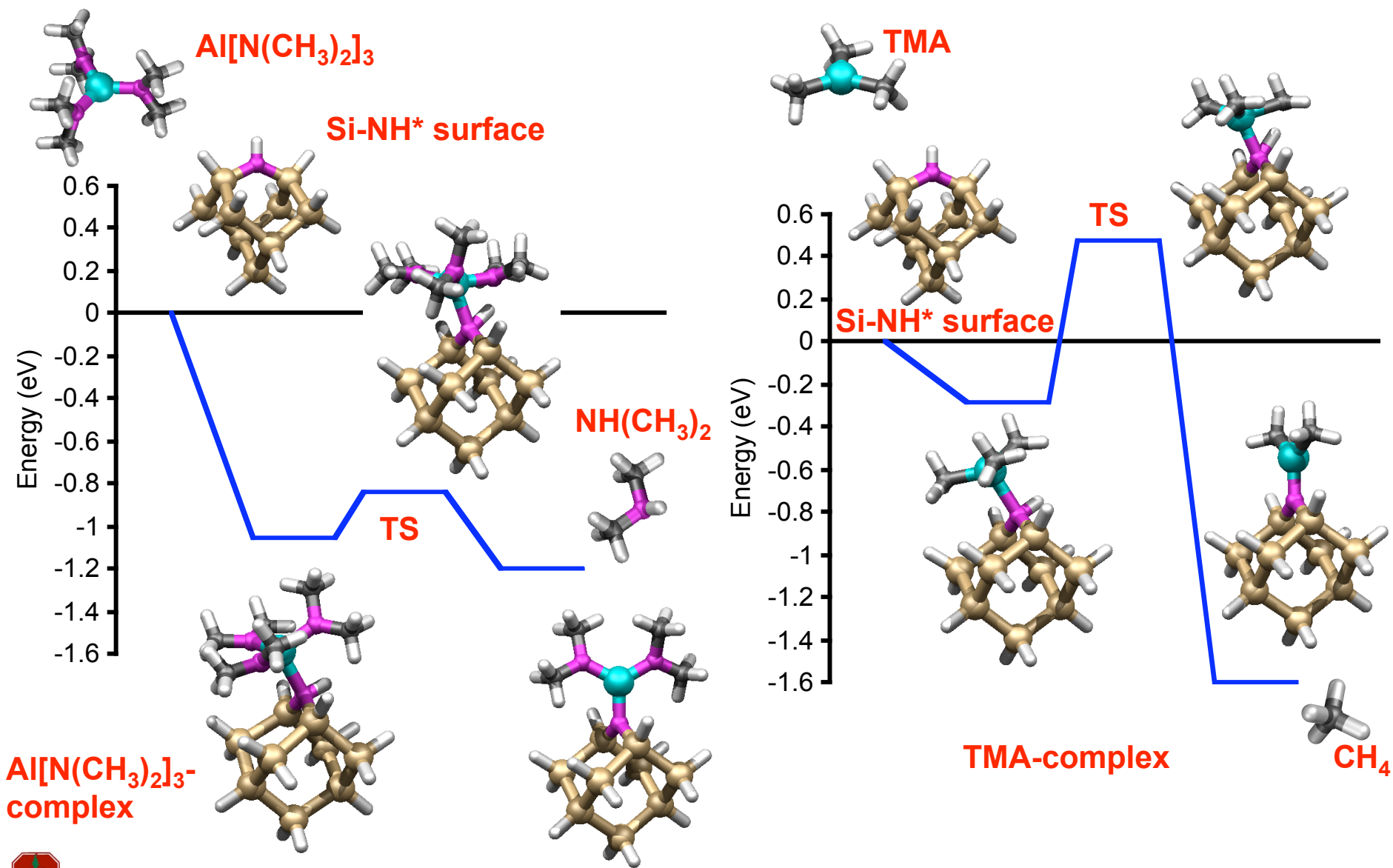
Alkylamide ALD on Amine Terminated SAM?



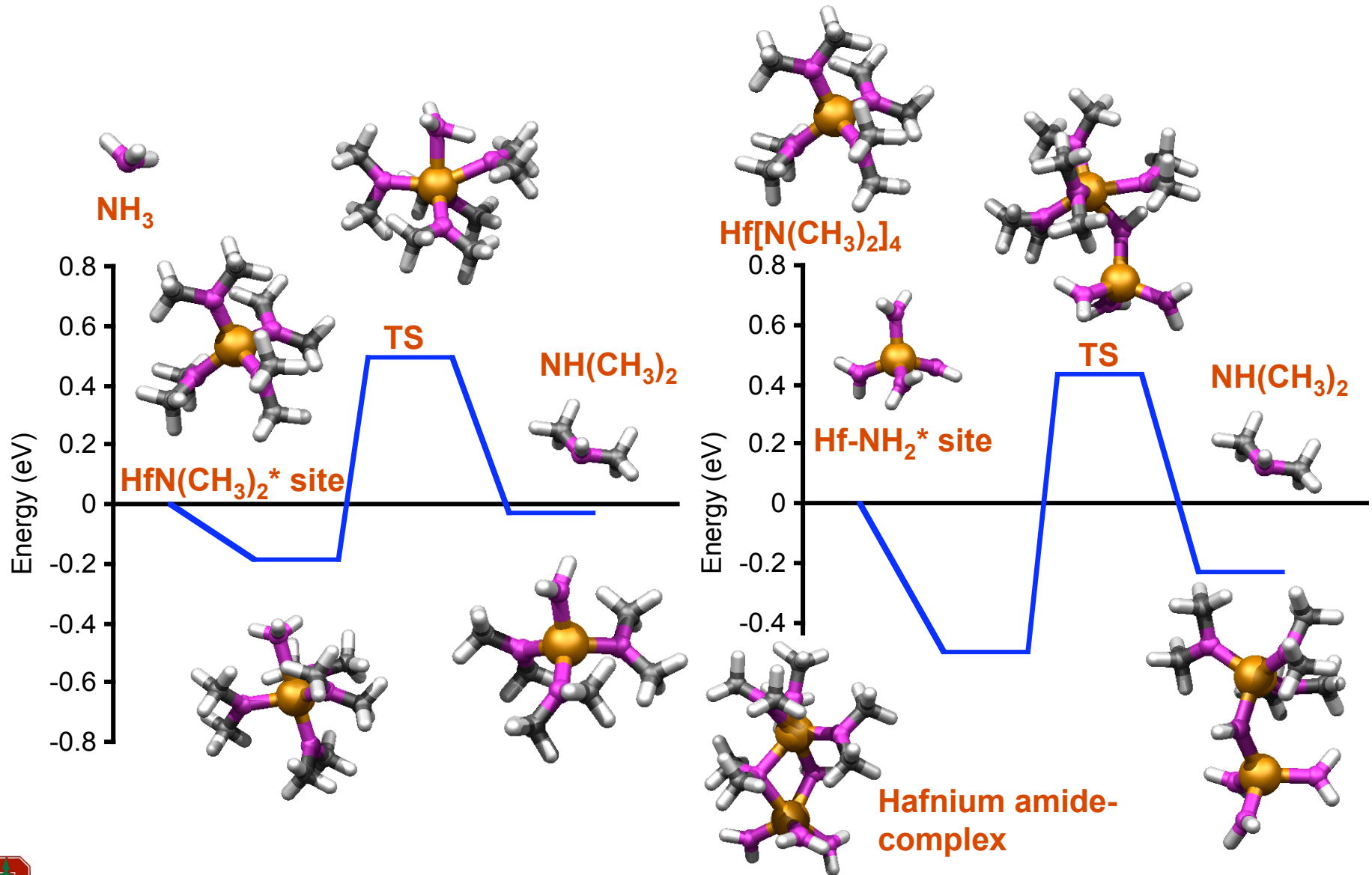
- Alkylamide precursor should allow even lower growth T .
- Other metal reactions for forming contacts to molecular electronic devices?
- ALD on NH terminated surfaces?



HfO₂ ALD on NH* Terminated Si and Ge



Hf Nitride or Oxynitride ALD?



Conclusions

- Details of high-K ALD mechanisms predicted including kinetics
- ALD temperature is determined by barrier relative to trapped intermediate or desorption of byproducts (for alkoxides)
- Submonolayer growth due to a combination of sterics, desorption of precursor and limited surface reactive sites.
- Precursors should have exothermic reactions for ALD reactions: Chlorides a poor choice
- Alkylamides are most promising high-K ALD precursors: low T, low contamination, best choice for area-selective ALD
- Substrates only affect initial ALD reaction
- Other substrates (Ge, nitrides, organics) work for these ALD chemistries if they are OH functionalized or NH functionalized (for alkylamide precursor)



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