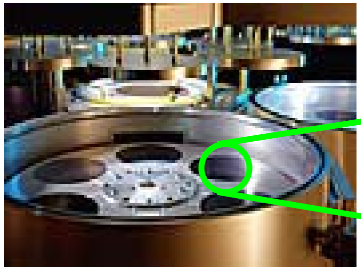
Simulation of High-K Gate Deposition

Charles B. Musgrave

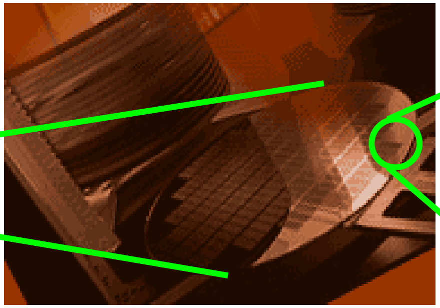
Yuniarto Widjaja, Gillian Gao, Joseph Han, and Juan Senosiain

Departments of Chemical Engineering & Materials Science and Engineering

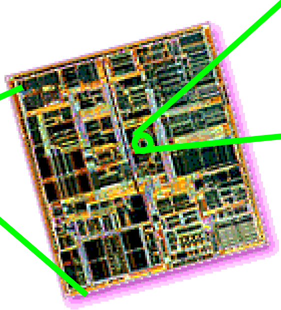
Stanford University, Stanford, CA 94305



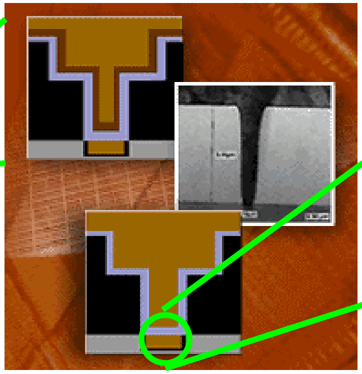
(www.novellus.com)



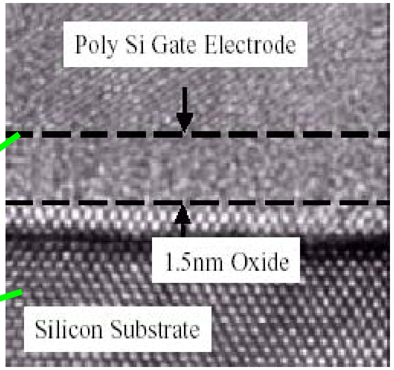
(www.novellus.com)



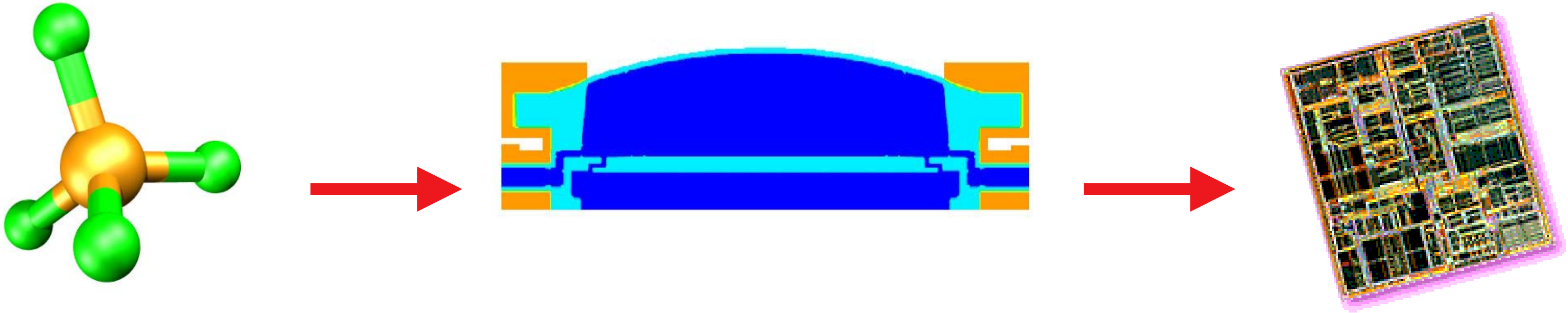
(www.intel.com)



(www.novellus.com)

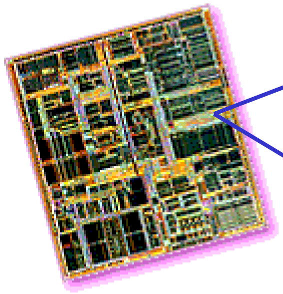


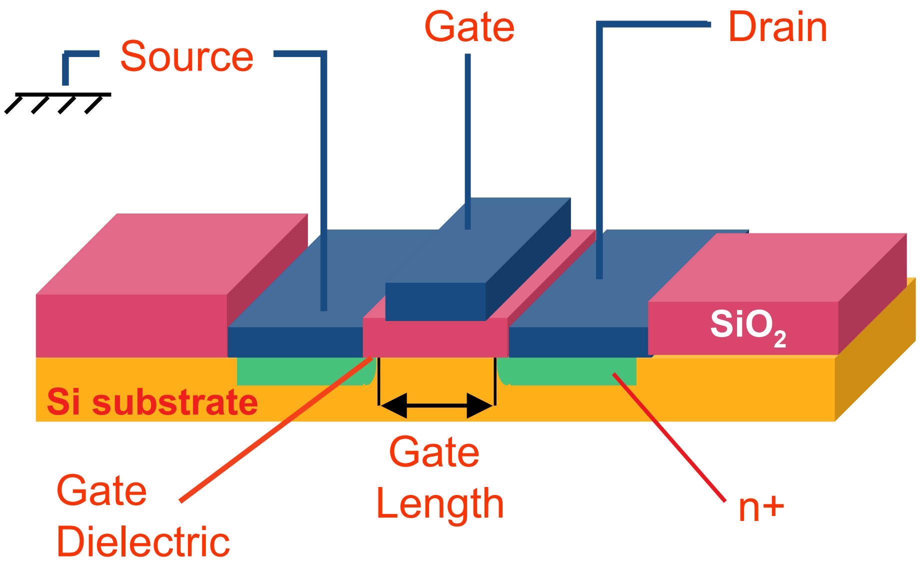
Yamaguchi, APL, 2002

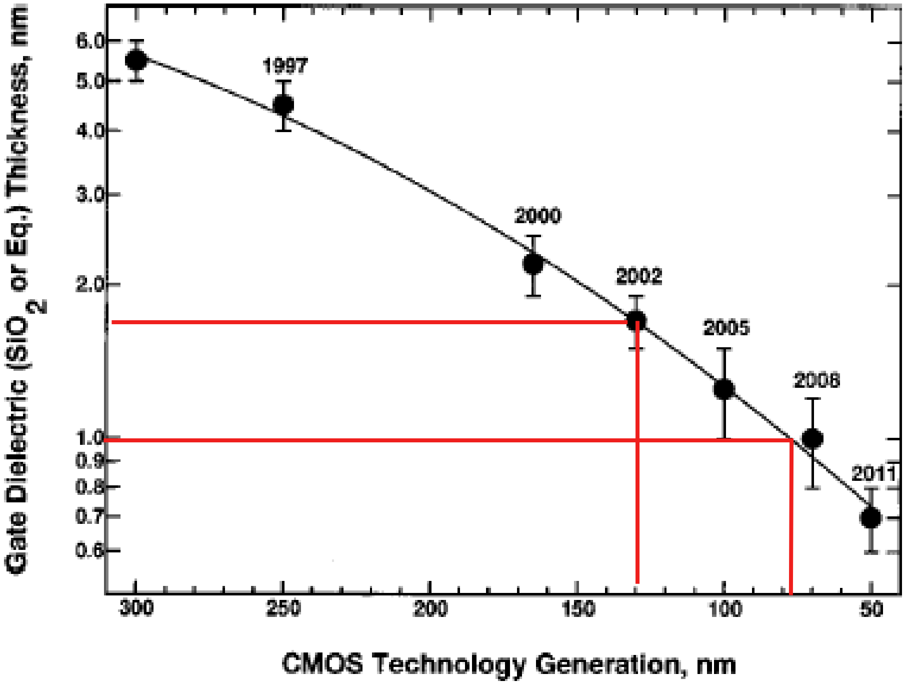


MOSFET Scaling

- Metal-Oxide-Semiconductor (MOS) structure







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

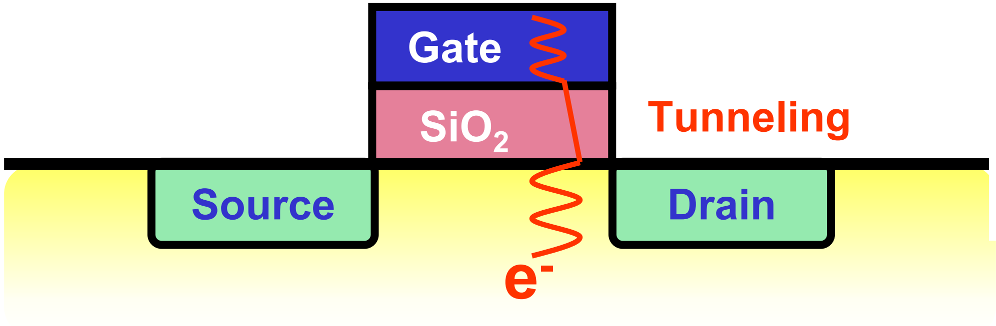
$$C = \frac{\kappa \varepsilon_0}{t}$$

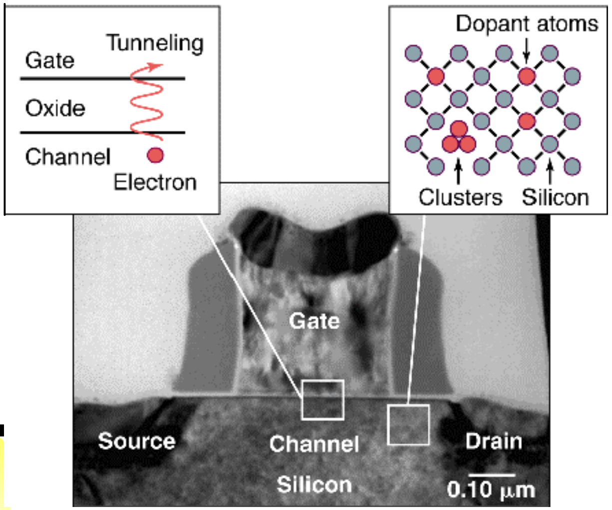
As MOS gates are made shorter they must be made thinner to control the channel.

Gate Leakage Due to Electron Tunneling

Current Technology:

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





P.A. Packan, Science, 1999

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.

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

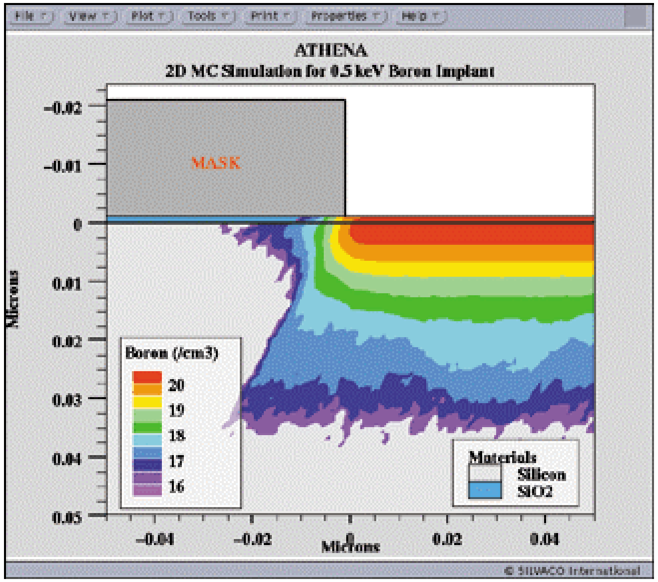
High-K Choices

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**

- ZrO_2 ,HfO_2 ,and Al_2O_3 are favorable candidates for the gate dielectric
  - High-k
  - Stable with respect to 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 SiO_2

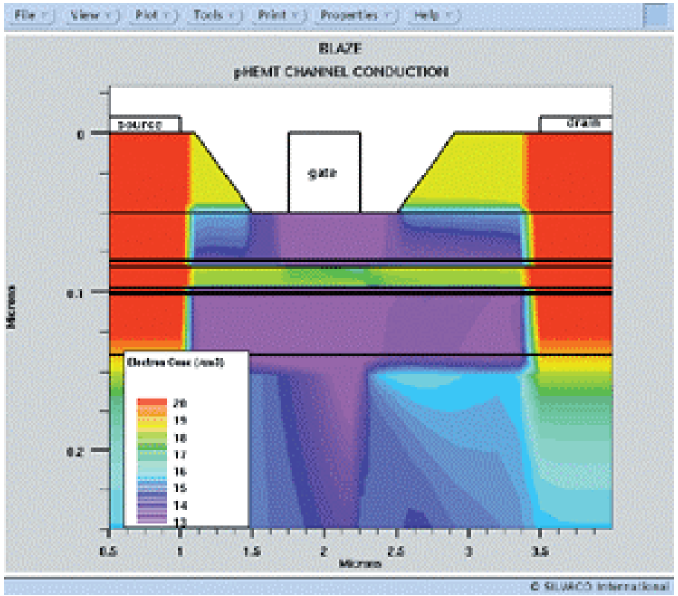
Traditional TCAD

Process Simulation



www.silvaco.com

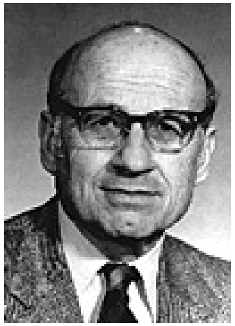
Device Simulation



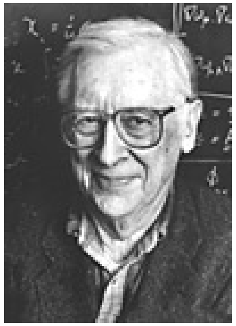
ITRS Modeling and Simulation Challenges Through 2007:

1. A succession of modeling tools that marry atomistic effects with present day continuum software tools.
2. Methods and algorithms that will allow prediction of CMOS limits. Quantum based simulators.

Quantum Chemistry



Walter Kohn
USA
University of California
Santa Barbara, CA



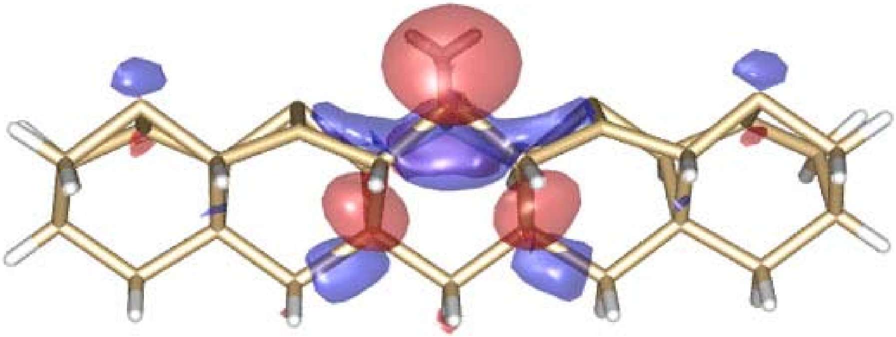
John Pople
USA, Great Britain
Northwestern University
Evanston, IL

"for his development of the density-functional theory"

"for his development of computational methods in quantum chemistry"

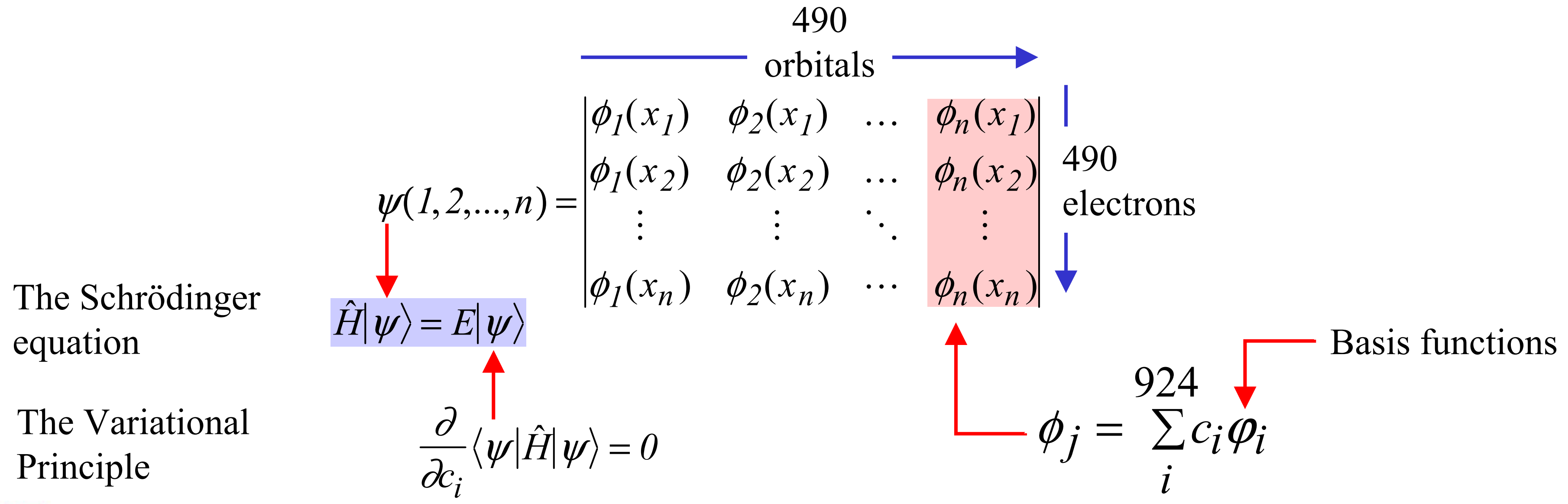
The Electronic Wave Function

This is one orbital of ammonia adsorbed on a cluster representing the silicon surface.



NH_3 on $Si_{33}H_{28}$

Here the wave function is the determinant of a 490x490 matrix (240,100 elements). Each element is a linear combination of 924 basis functions. The 924 basis coefficients for each of the 490 orbitals is found by minimizing the expectation value of the Hamiltonian.



$$\psi(1,2,\dots,n) = \begin{array}{cccc|c} \multicolumn{4}{c|}{\text{490 orbitals}} & \\ \hline \phi_1(x_1) & \phi_2(x_1) & \cdots & \phi_n(x_1) & \\ \phi_1(x_2) & \phi_2(x_2) & \cdots & \phi_n(x_2) & \text{490 electrons} \\ \vdots & \vdots & \ddots & \vdots & \\ \phi_1(x_n) & \phi_2(x_n) & \cdots & \phi_n(x_n) & \end{array}$$

The Schrödinger equation

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

The Variational Principle

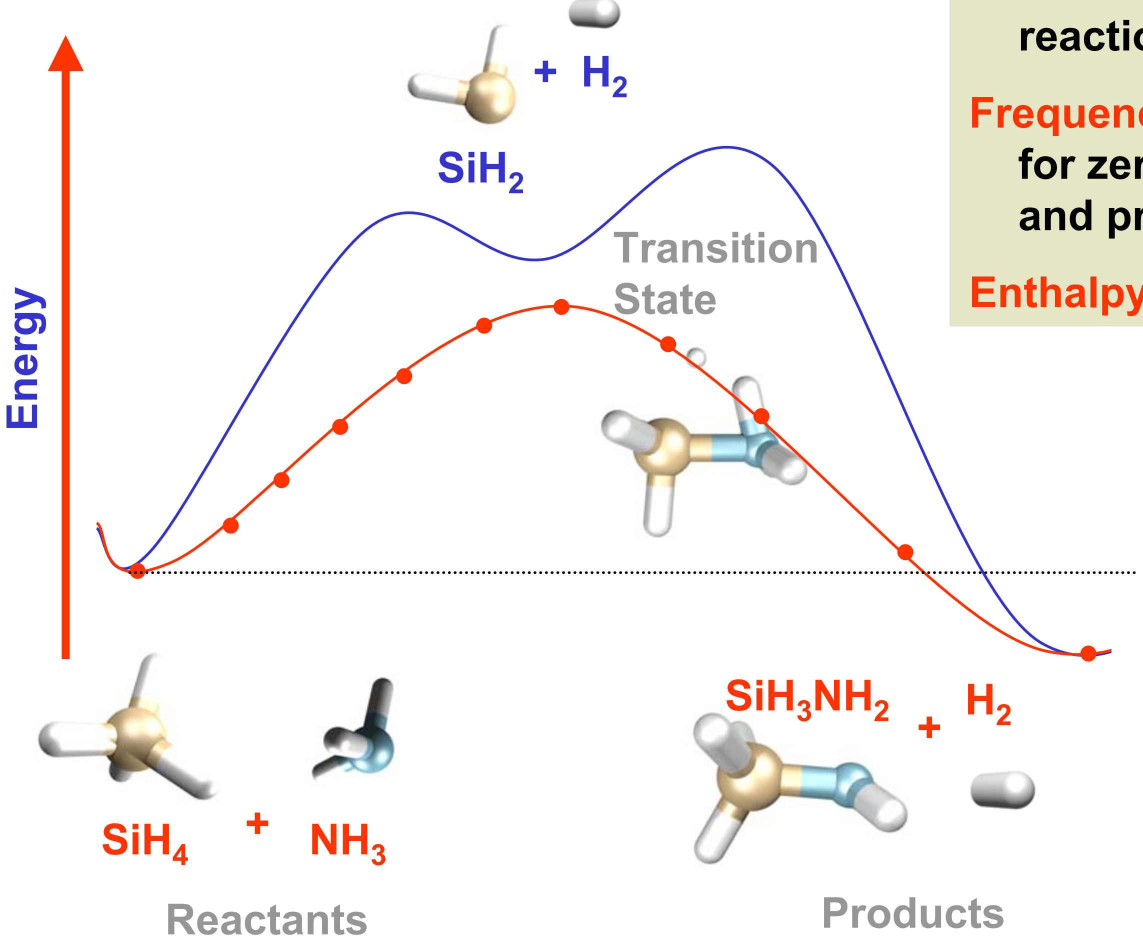
$$\frac{\partial}{\partial c_i}\langle\psi|\hat{H}|\psi\rangle = 0$$

Basis functions

$$\phi_j = \sum_{i}^{924} c_i \varphi_i$$

Potential Energy Surface

Competing reactions can be explored.



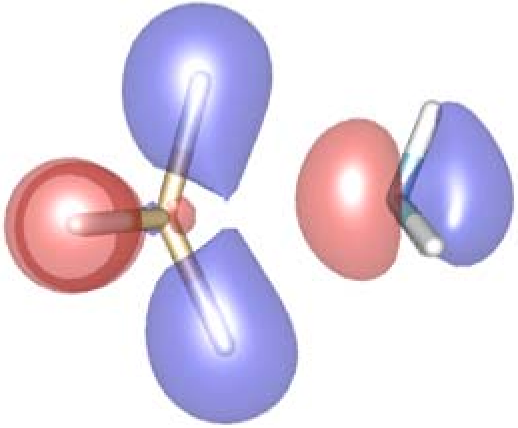
Reactants and products are local minima.

Transition states are saddle points.

Activation barrier determines the rate of reaction.

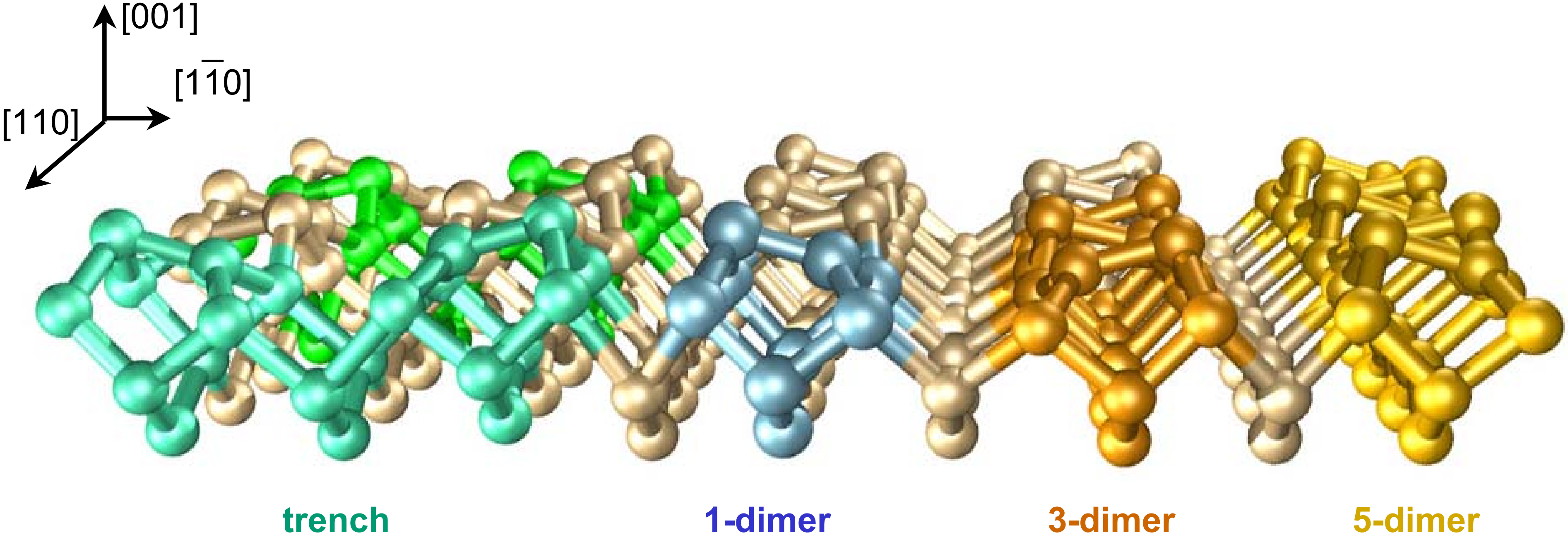
Frequencies can identify species, are used for zero-point and thermal corrections, and pre-exponential factors.

Enthalpy of Reaction driving force for rxn.



Surface Reaction Modeling

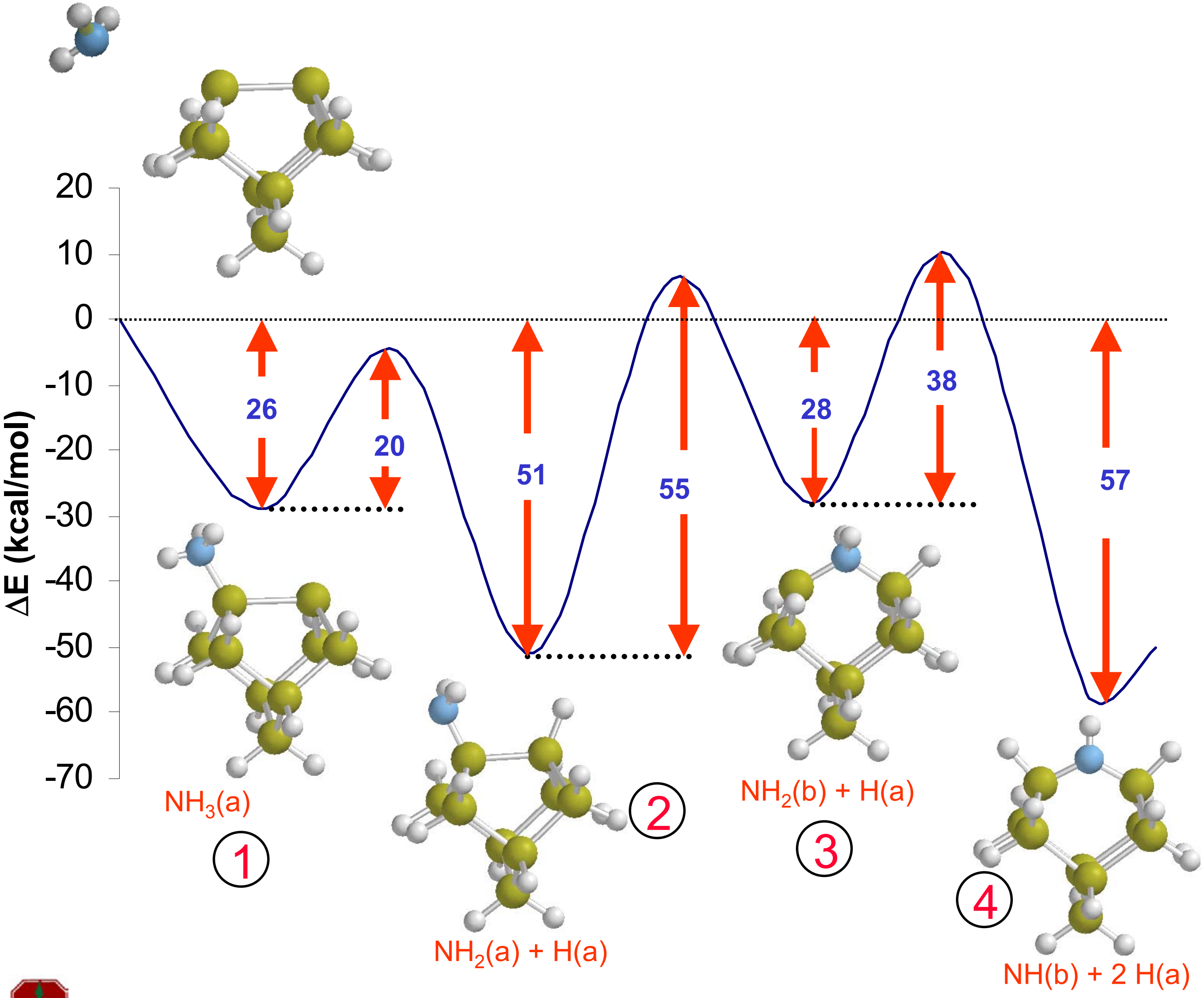
- Cluster approximations are used to model the surface reactive sites



- Cluster models: 1-dimer (blue), 3-dimer (copper), 5-dimer (gold), V-trench, and Λ-trench (green).
- Hydrogen termination.

Approximation: The chemistry on the cluster captures the chemistry of the surface

NH_3 on Si (100)-(2x1)

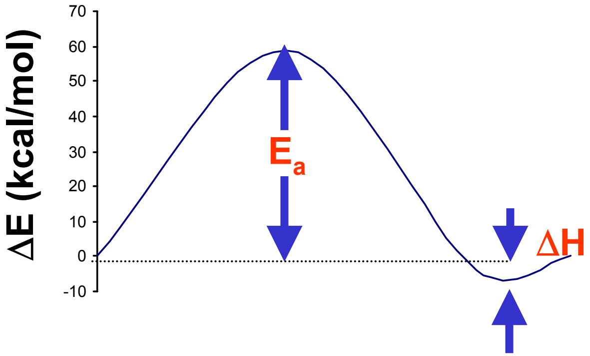


Insertion Mechanism:

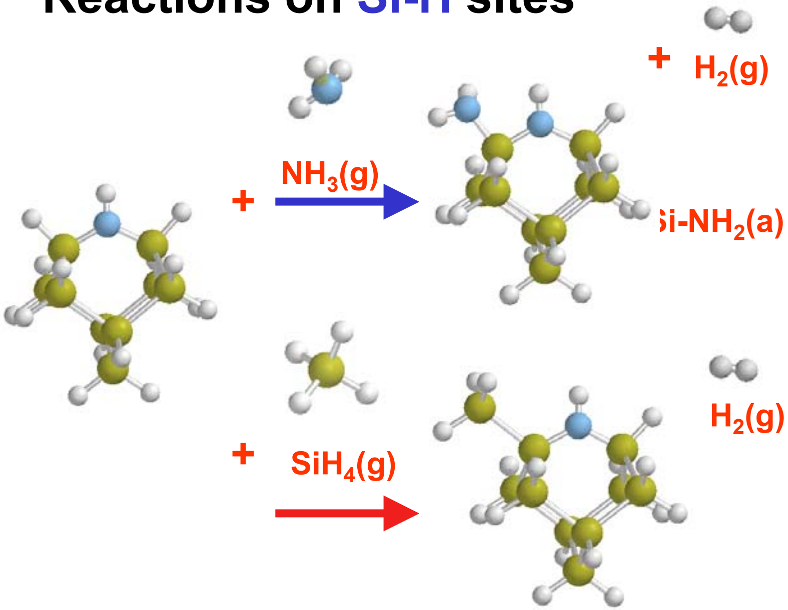
1. **$NH_3(g)$ initially adsorbs on the "down" Si atom.**
2. **$NH_3(a)$ dissociates into $NH_2(a)$ and H(a).**
3. **$NH_2(a)$ inserts into Si-Si dimer bond.**
4. **$NH_2(a)$ dissociates into NH(a) and H(a).**

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

Subsequent Nitride Growth



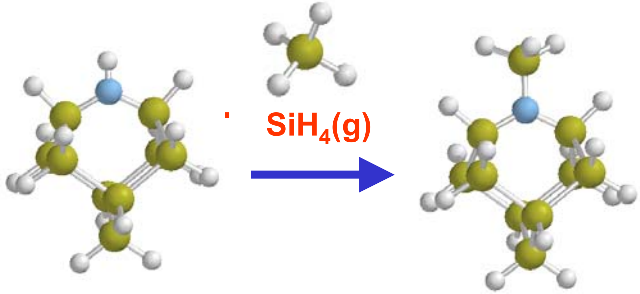
Reactions on Si-H sites



E_a = 59

E_a = 75

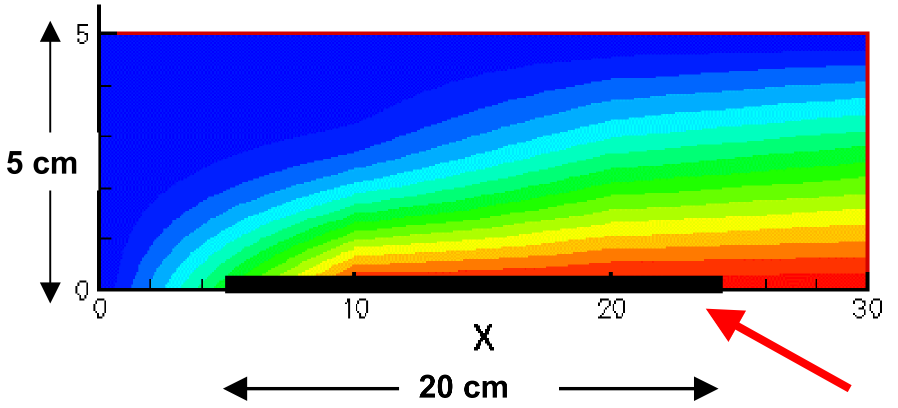
Reactions on N-H sites



E_a = 49

Reactor Modeling

- Model CVD reactor using simple geometry (2D channel)
- Couple transport, gas-phase and surface reactions
- Use predicted barriers for the gas-phase and surface reactions



Reactants

SiH_4, NH_3, N_2O

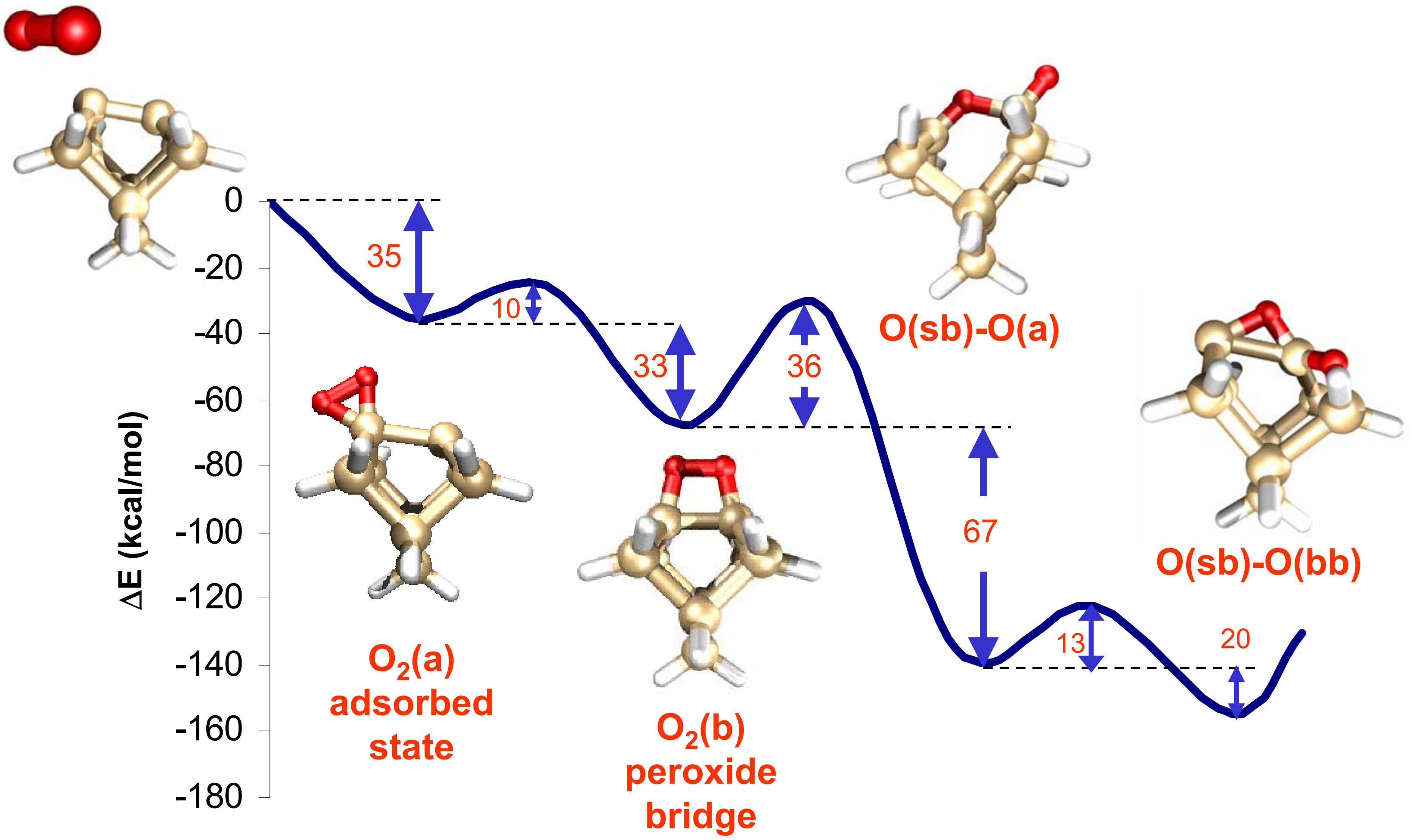
By-products

Wafer

MOTOROLA

Initial Oxidation Reaction Mechanism

Reaction is all down hill: Why is the oxidation slow?



The ALD Process

Self-terminating Reactions

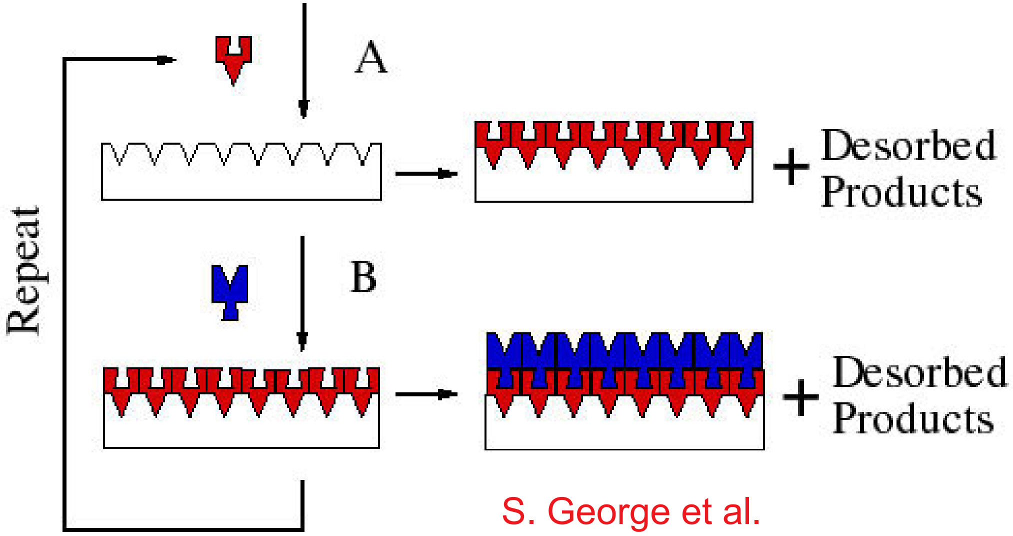
- ALD consists of an alternating sequence of self-terminating reactions.
- Ideally, each step should form a monolayer.

Advantages of ALD

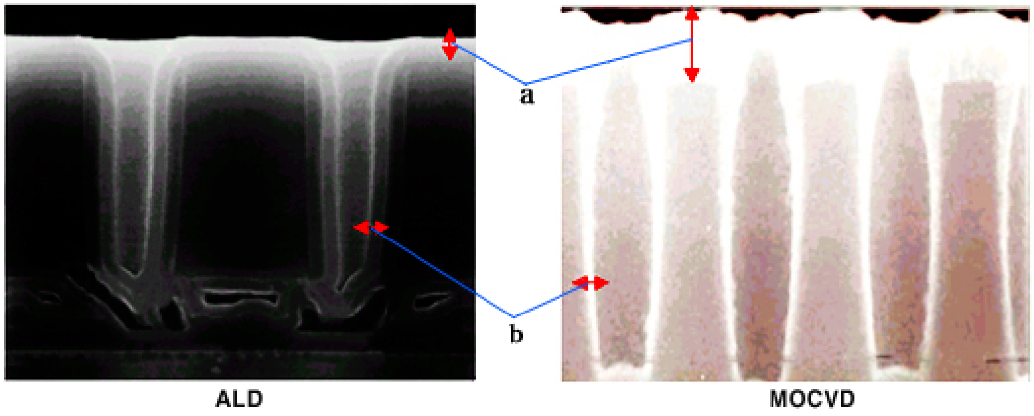
- Excellent conformality (step coverage >95%)
- Excellent film thickness control –allows for growth of extremely thin films
- Low processing temperatures
- High purity films

ALD Issues

- Process is slow
- Submonolayer coverage
- Interlayer SiO_2 below ZrO_2



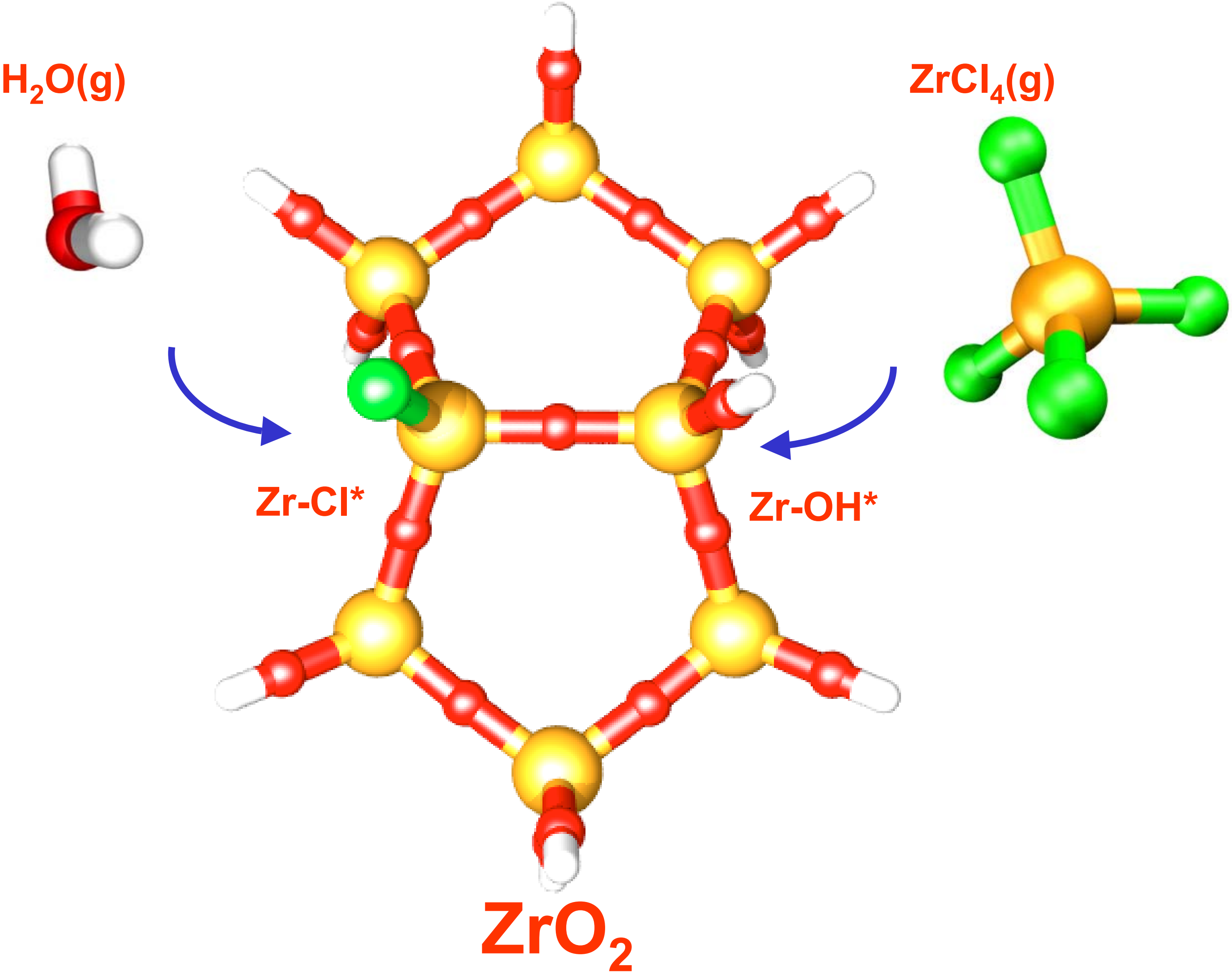
S. George et al.



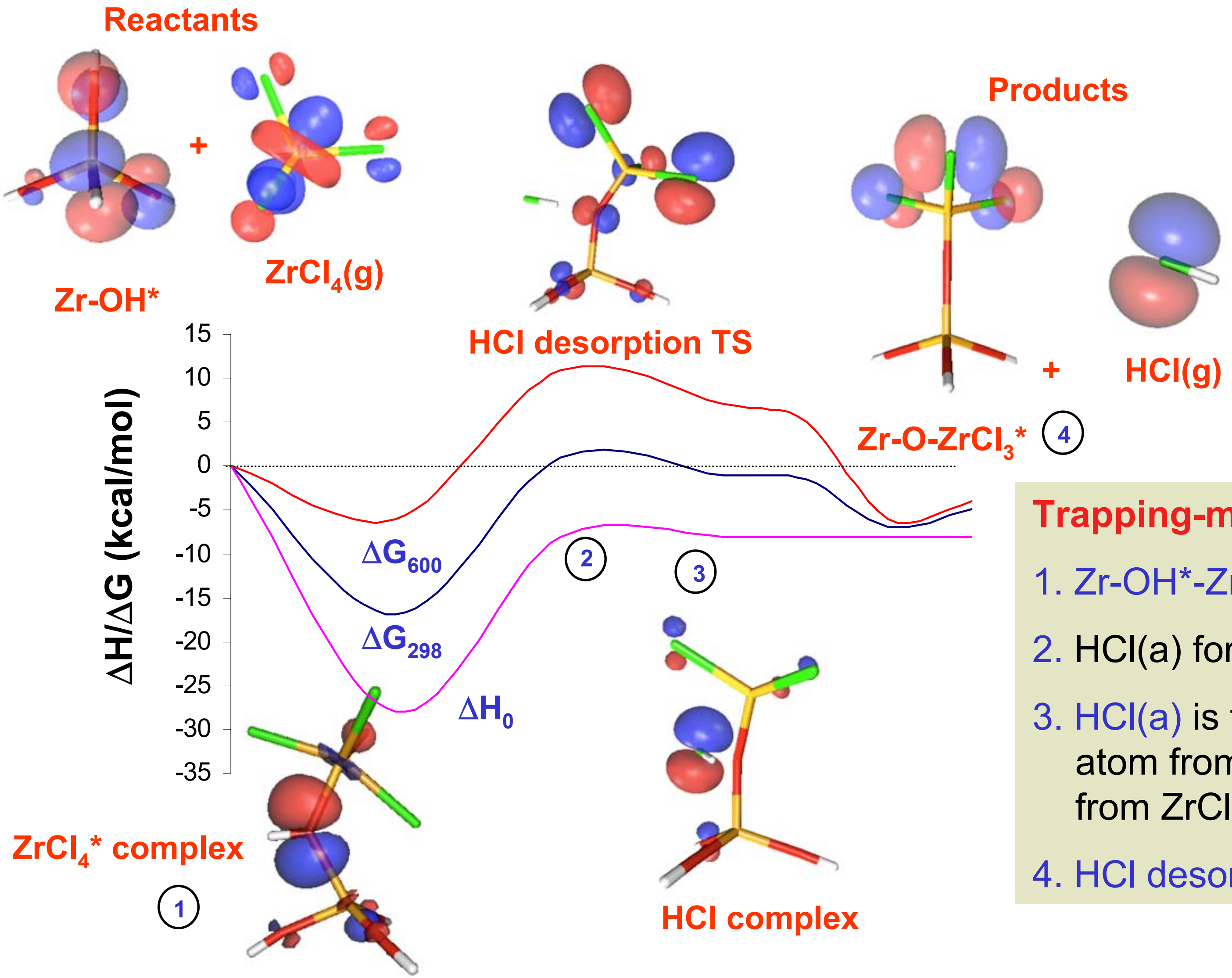
$$\text{Step Coverage} = \frac{b}{a} \times 100(\%)$$

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

Zirconium Oxide ALD



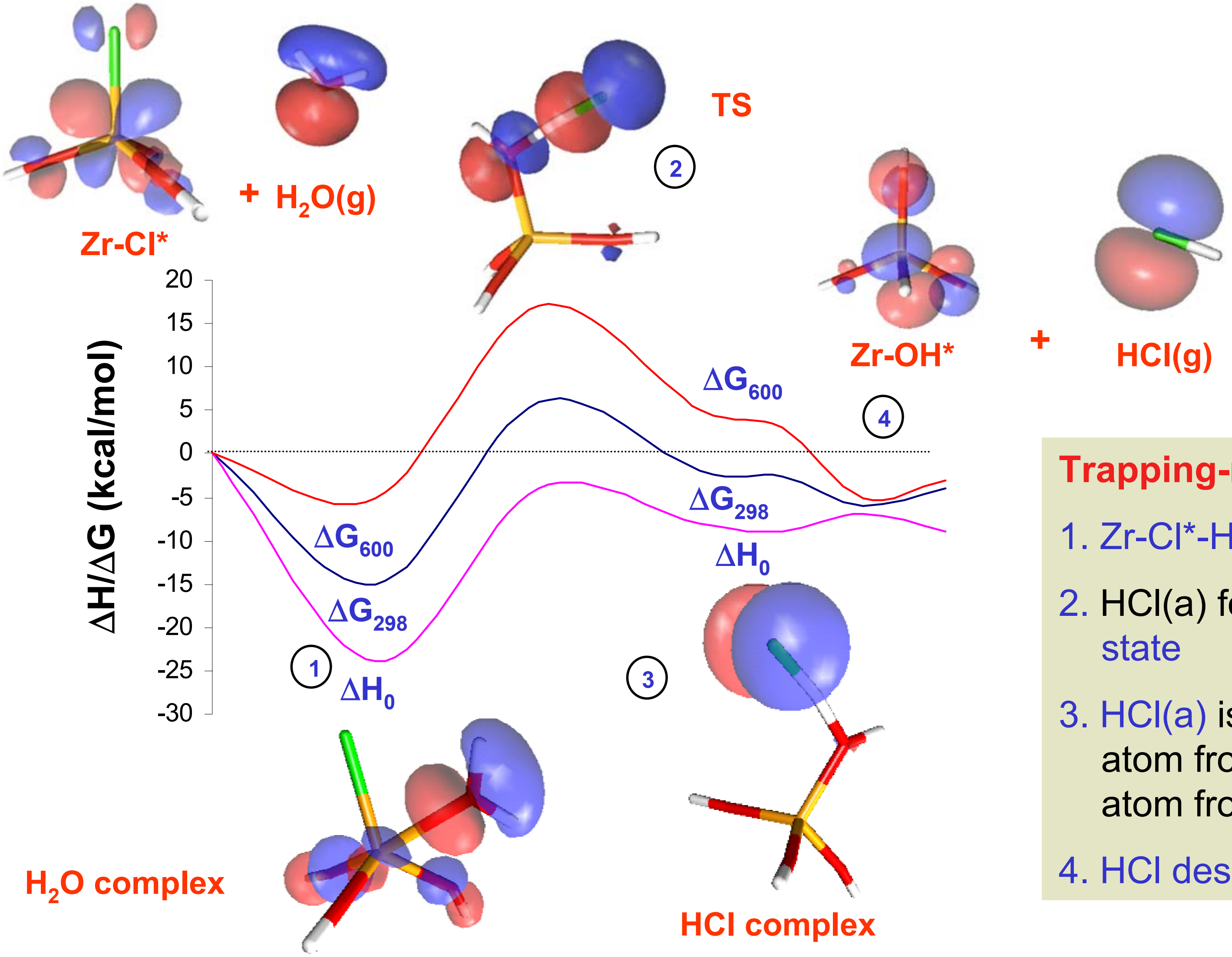
ZrO_2 ALD Reaction with Zr-OH* Sites



Trapping-mediated pathway:

1. Zr-OH*-$ZrCl_4$ complex is formed
2. HCl(a) formation transition state
3. HCl(a) is formed from one H atom from H_2O and one Cl atom from $ZrCl_3$
4. HCl desorbs

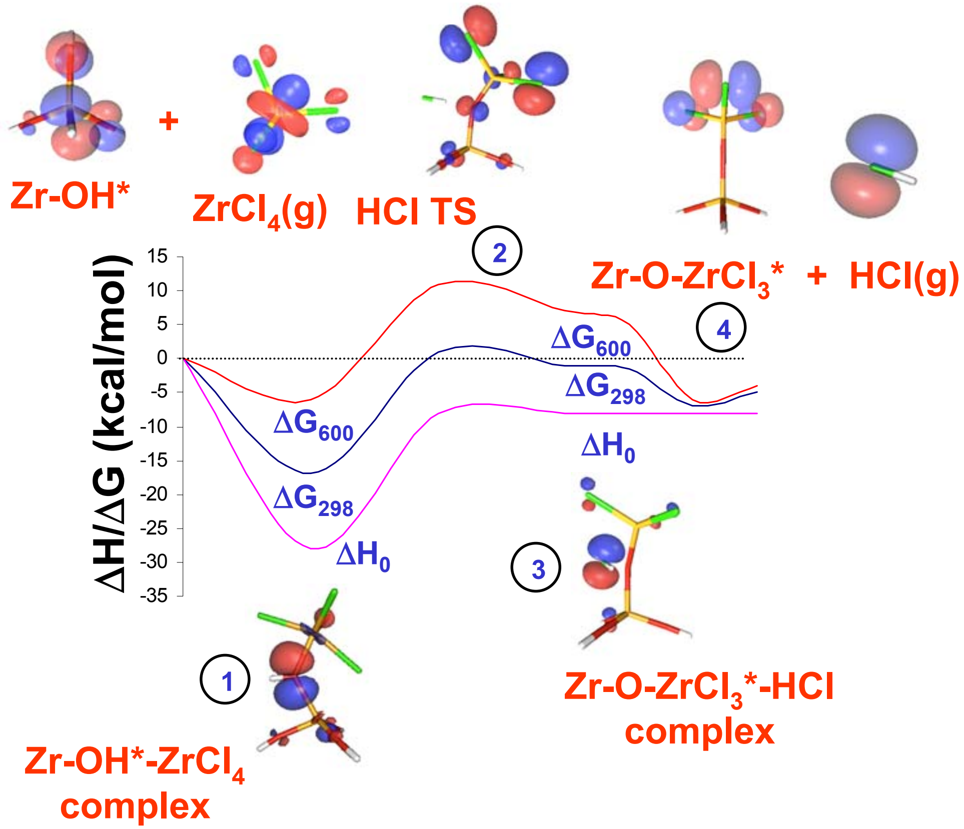
ZrO_2 ALD Reaction with Zr-Cl* Sites

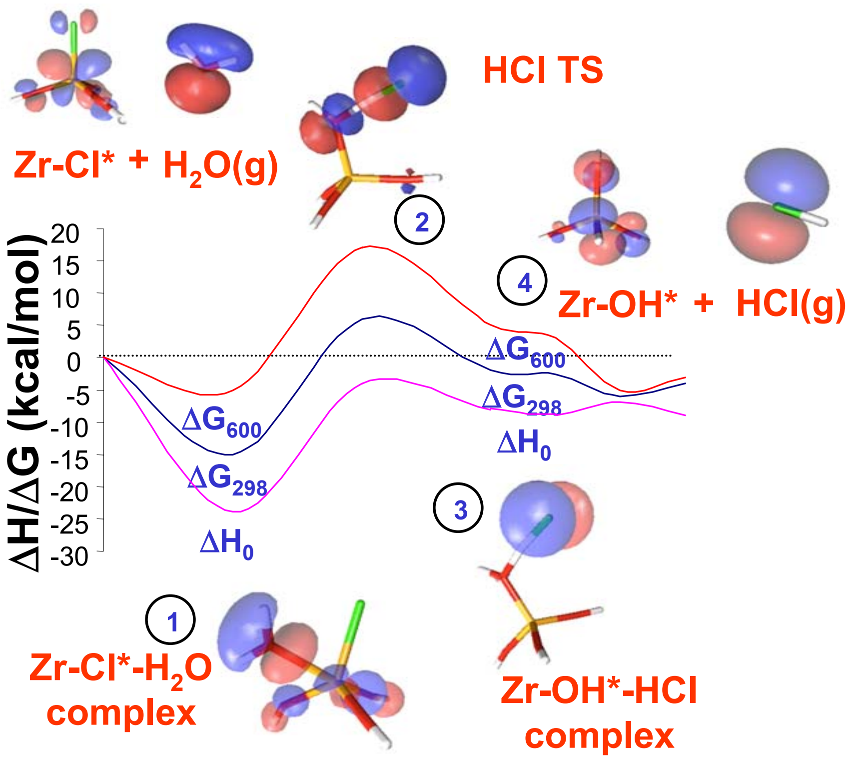


Trapping-mediated pathway:

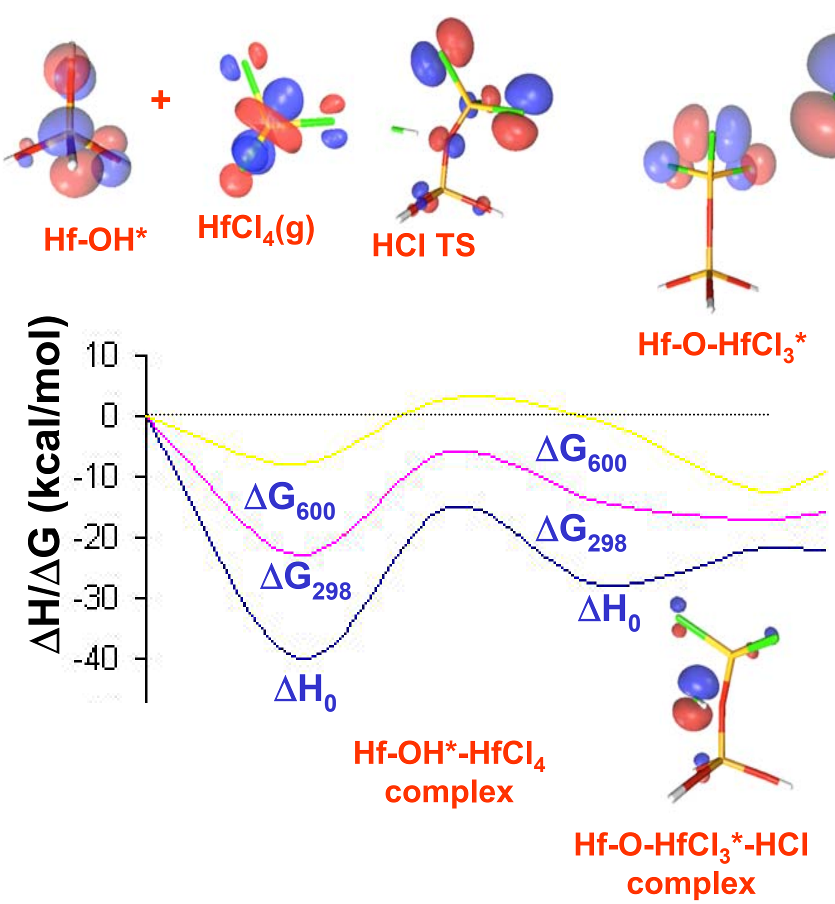
1. Zr-Cl*-H_2O complex is formed
2. HCl(a) formation transition state
3. HCl(a) is formed from one H atom from H_2O and one Cl atom from $ZrCl_3$
4. HCl desorbs

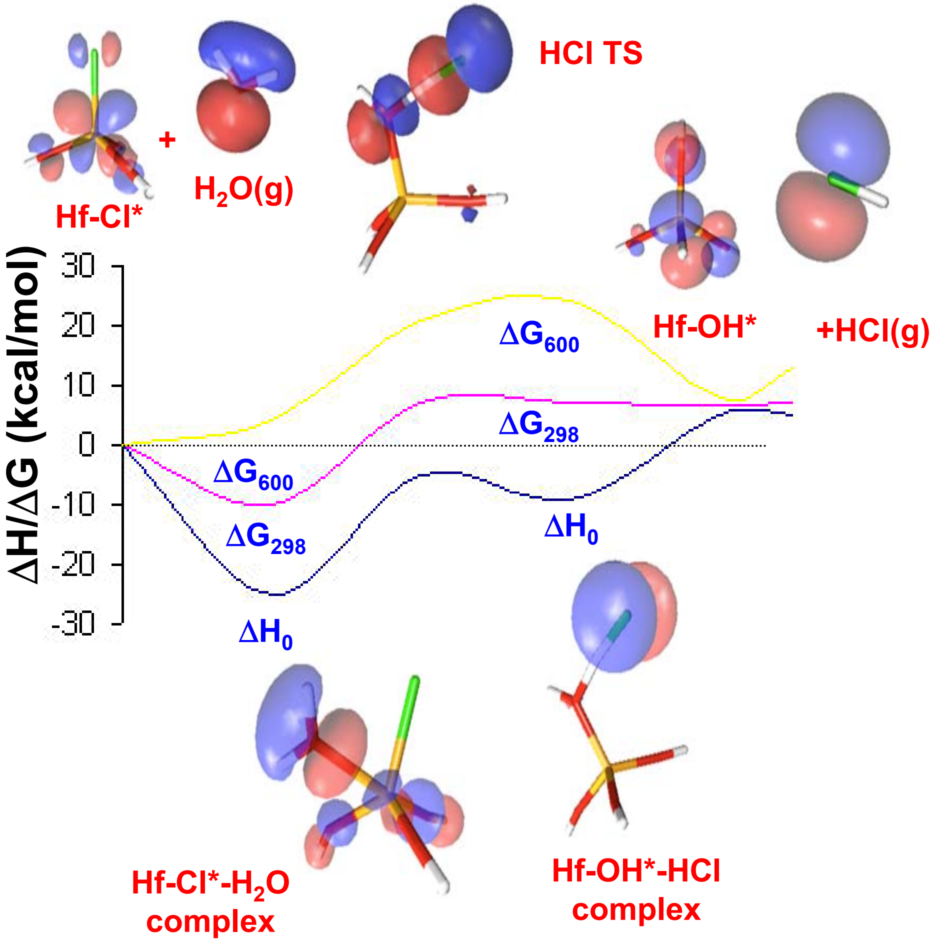
Comparison of the 1st & 2nd Half-reactions of ZrO_2 ALD



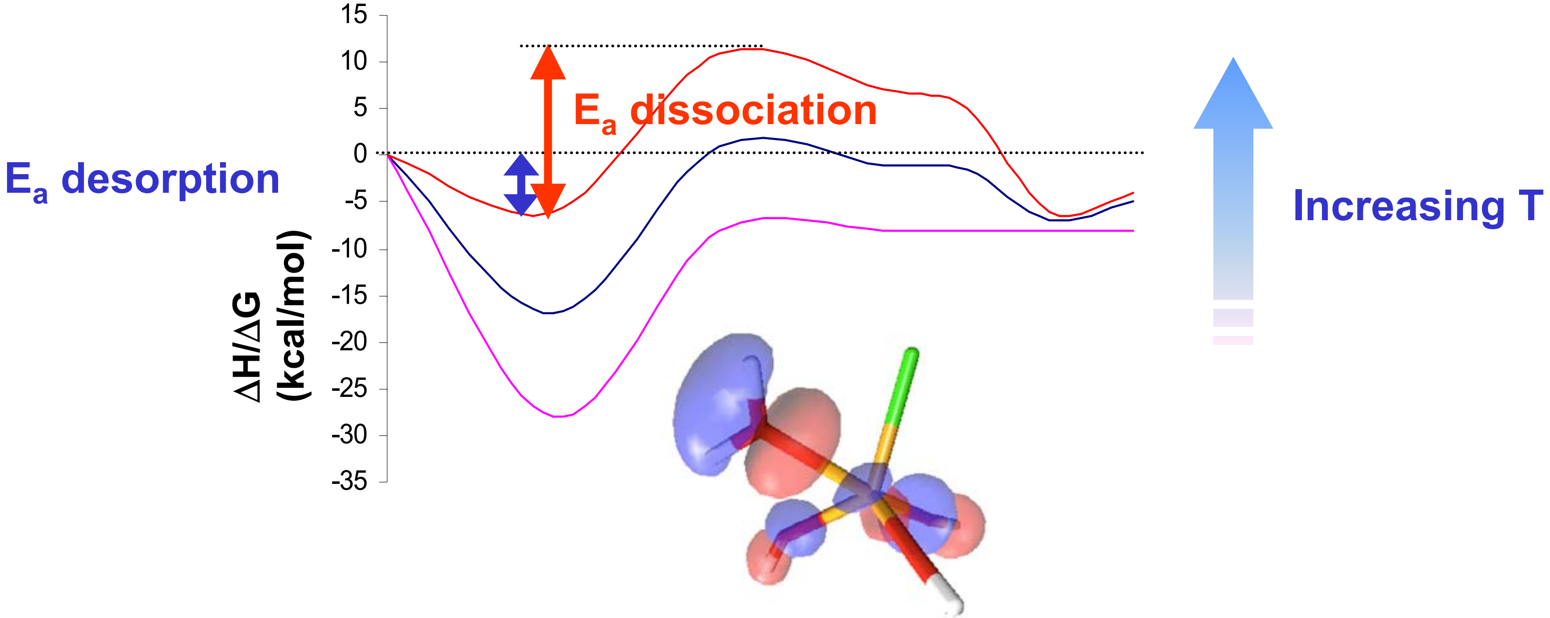


Comparison of the 1st & 2nd Half-reactions of HfO_2 ALD



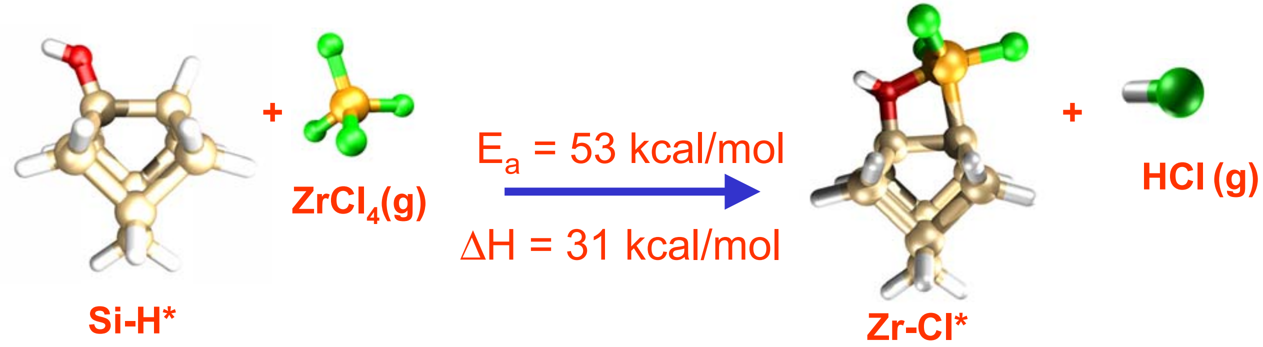


Partial Monolayer Growth

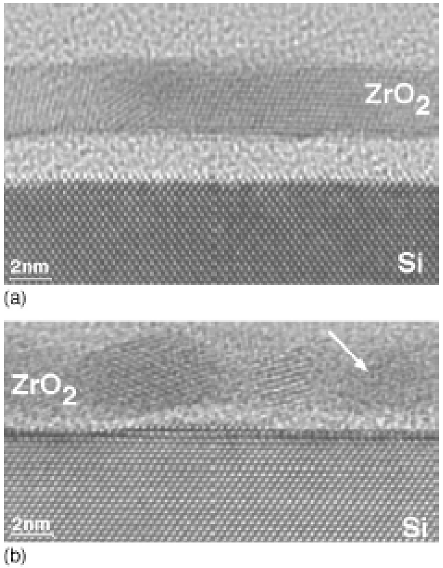


- Raising the temperature raises new issues:
  - Desorption becomes more favorable than dissociation
  - This results in less than a monolayer coverage per cycle.
    - Solution: increase the precursor pressure
  - Low-thermal budget processing might be desired

Reactions on H-terminated Surface

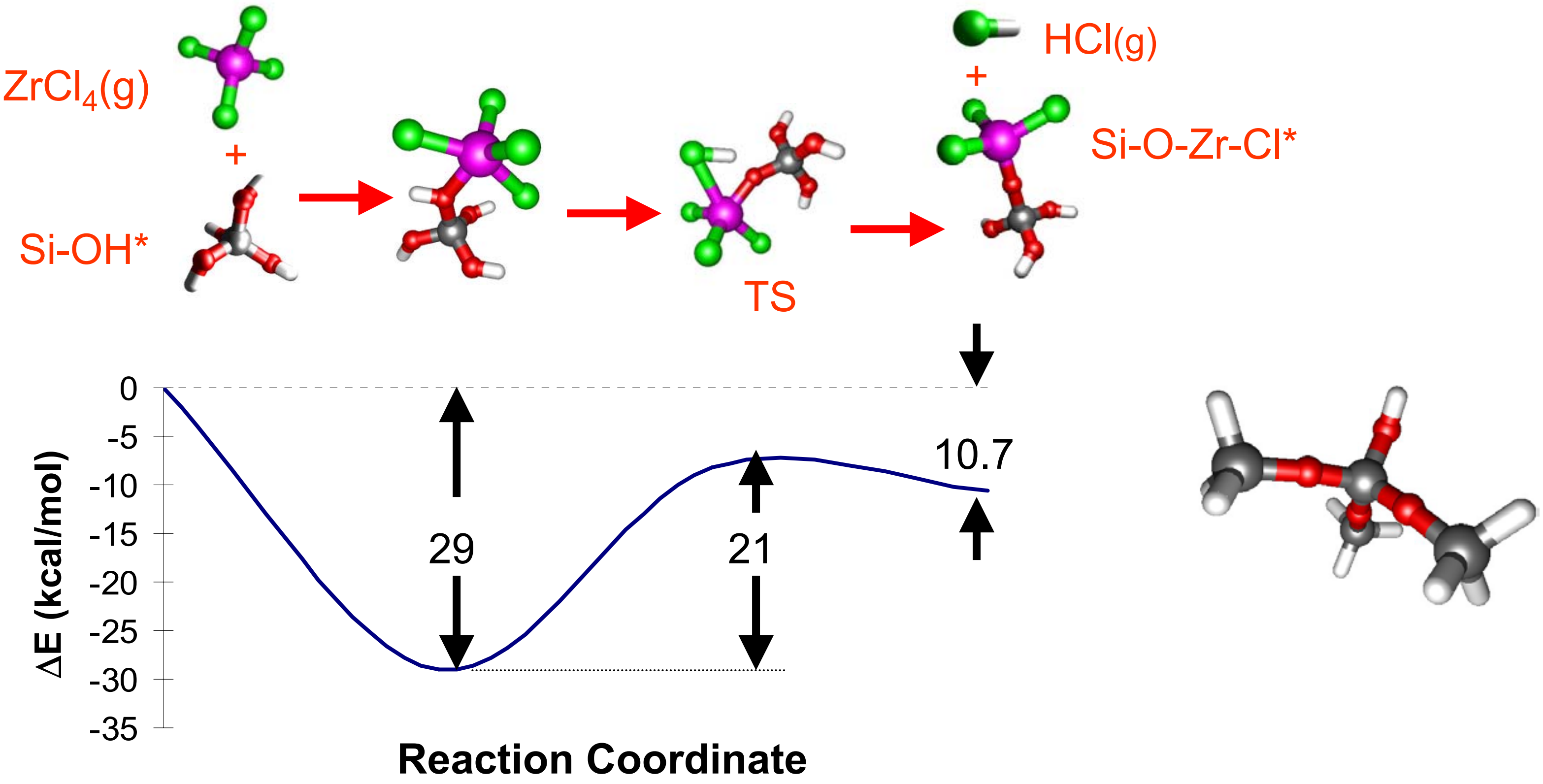


- Reaction of **$ZrCl_4(g)$** with the **Si-H*** has a high activation barrier and endothermicity.
- Reactions on the **H-terminated surface** will proceed slowly. This agrees with experimental results of Copel *et al*. (APL, 2000)



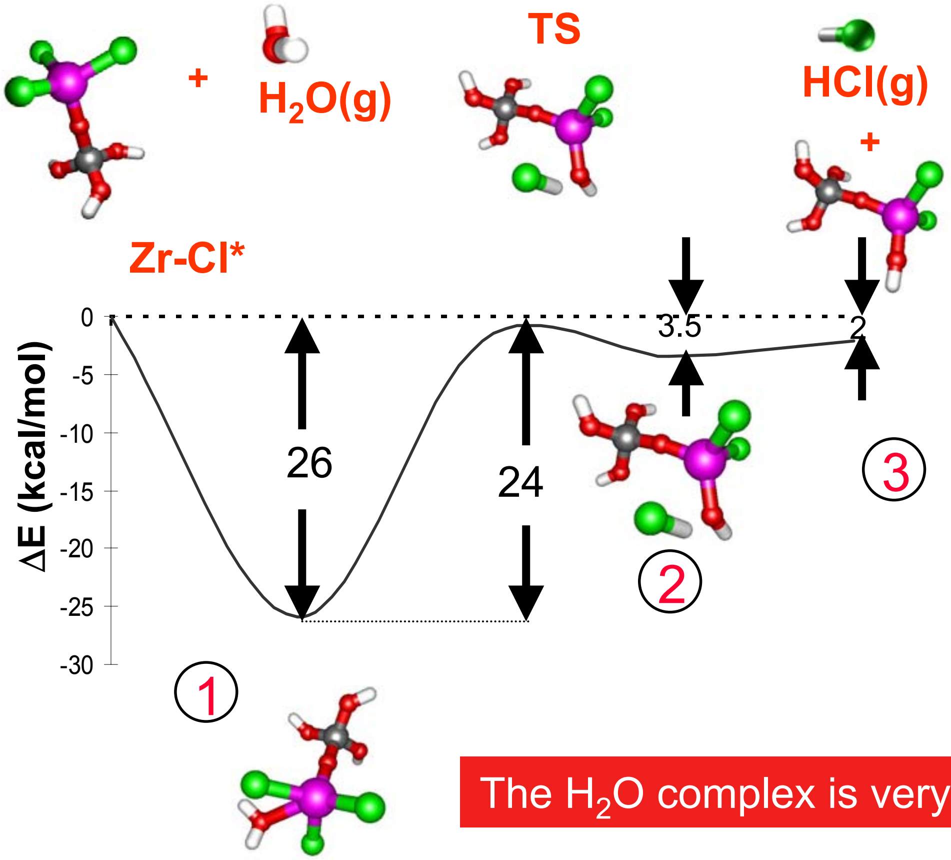
Copel et al., APL, 2000

Reaction of of $ZrCl_4$ on OH Terminated SiO_2



- $ZrCl_4$ reacts with Si-OH* surface sites to form a Si-OH-$ZrCl_4$ intermediate, followed by HCl evolution and formation of a Si-O-Zr-Cl* surface site

Reaction of H_2O with the Zr-Cl* Surface Site



The H_2O complex is very stable!

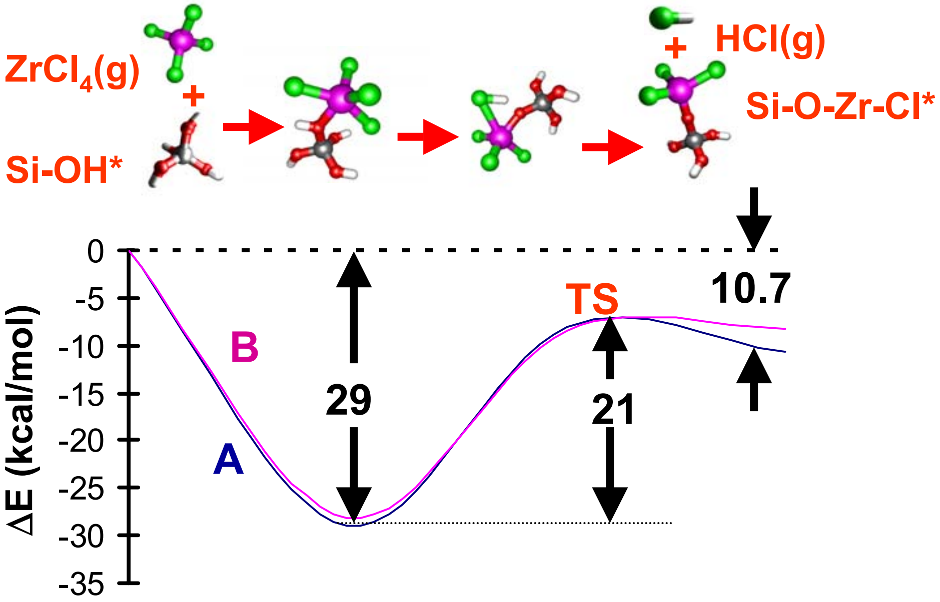
1. **Zr-Cl*-H_2O complex** is formed
2. **HCl(a)** is formed from one H atom from H_2O and one Cl atom from $ZrCl_3$
3. **HCl desorbs**

Comparison of ZrO_2 ALD Reactions on SiO_2 and ZrO_2

Half-reaction with $ZrCl_4$:

A: Si-OH* + $ZrCl_4$ = Si-O-Zr-Cl* + HCl

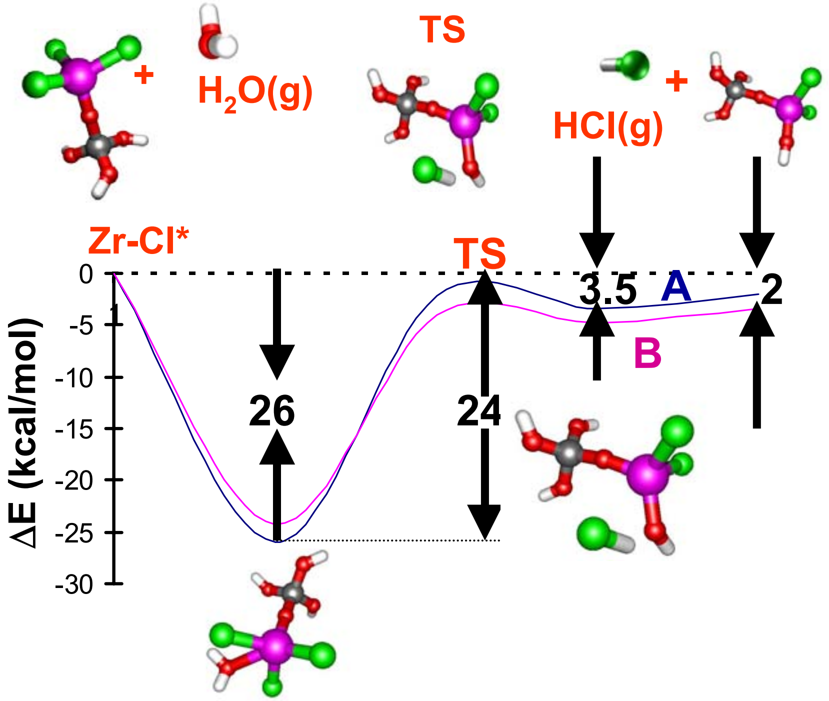
B: Zr-OH* + $ZrCl_4$ = Zr-O-Zr-Cl * + HCl



Half-reaction with H_2O:

A: Si-O-Zr-Cl* + H_2O = Si-O-Zr-OH* + HCl

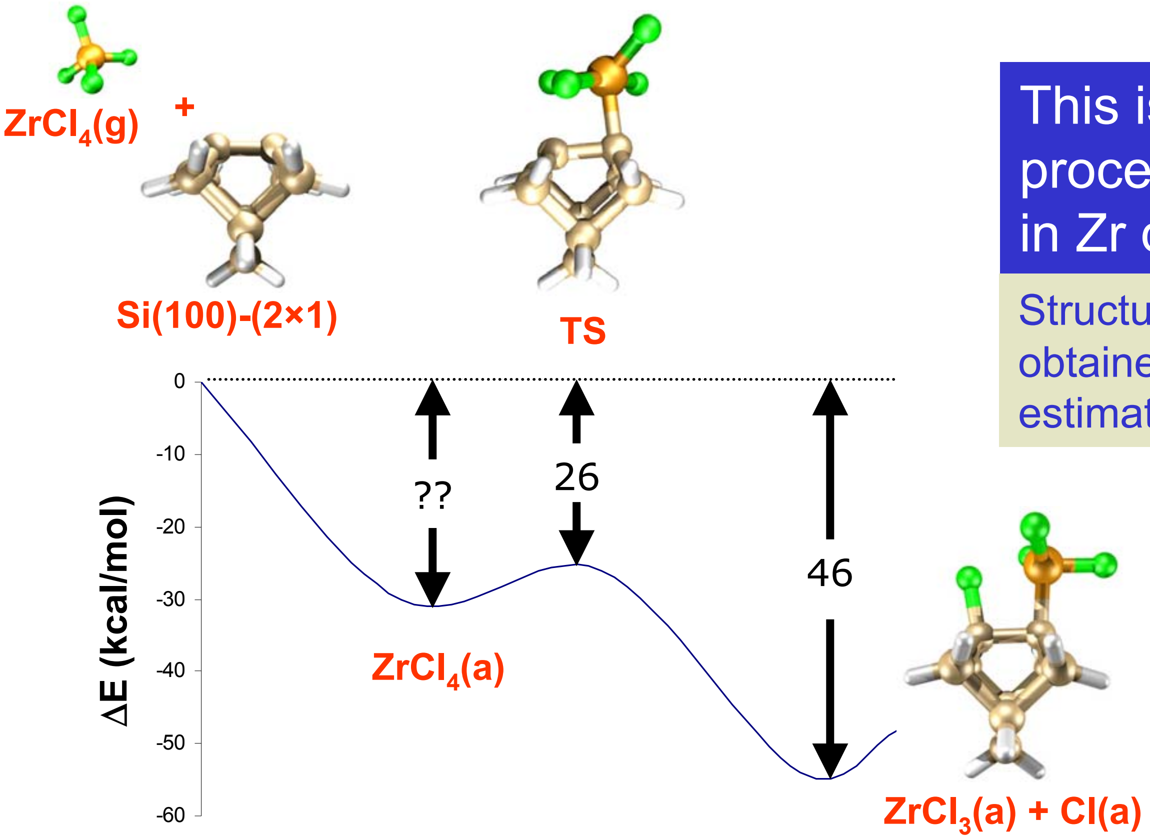
B: Zr-O-Zr-Cl* + H_2O = Zr-O-Zr-OH* + HCl



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

Issues: Trapping at the intermediate state.

ZrCl$_4$ on the Si(100)-(2x1) Surface

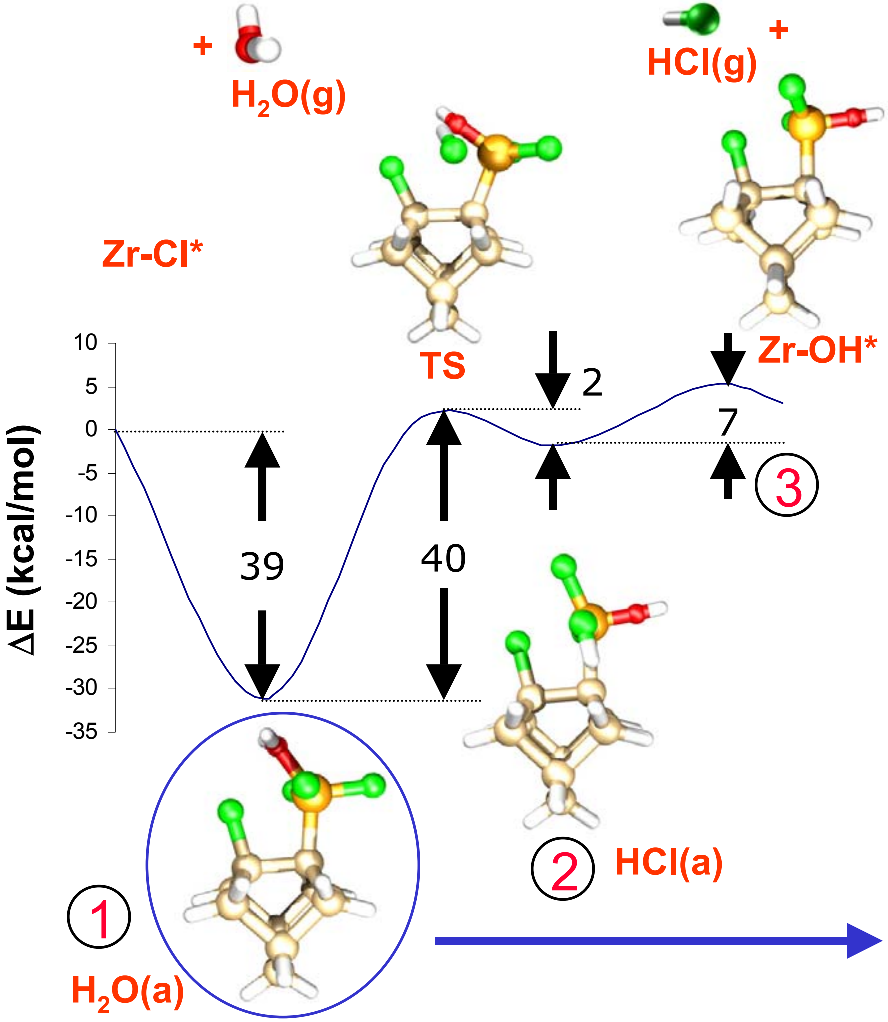


This is not the preferred process because it results in Zr directly bonded to Si

Structure of ZrCl$_4$(a) has not been obtained. However, ΔH_{ads} is estimated to be similar to E_{TS}

- ZrCl$_4$ dissociates into ZrCl$_3$(a) and Cl(a) on the Si(100)-(2x1) surface
- This results in **Zr-Cl*** and **Si-Cl*** surface sites

Reaction of H_2O with the Zr-Cl* Surface Site



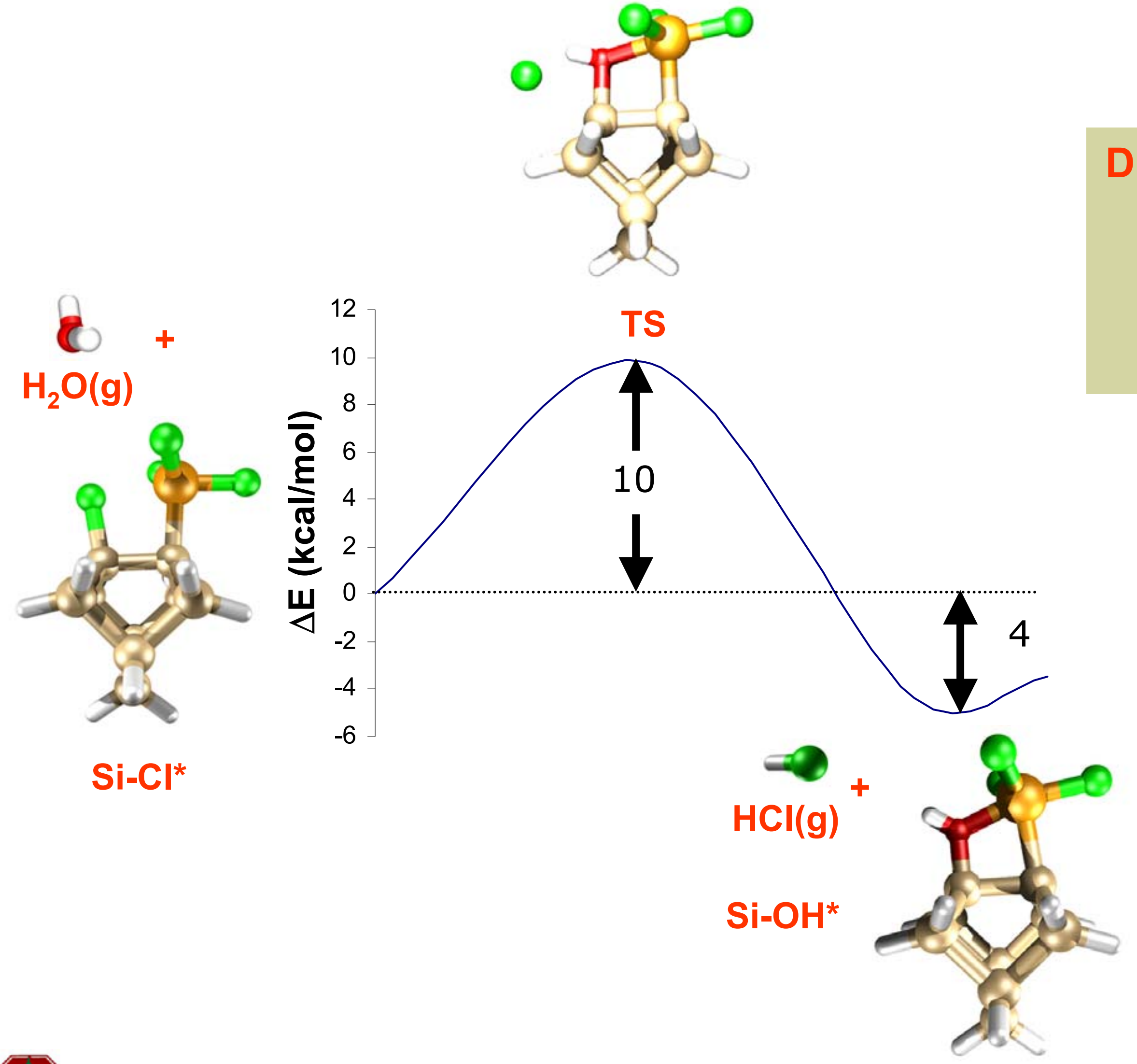
Reaction of **H_2O** with the **Zr-Cl*** site results in a **Zr-OH*** site in place of the **Zr-Cl*** site

Trapping-mediated mechanism:

1. **Zr-Cl*-H_2O complex** is formed
2. **HCl(a)** is formed from one H atom from H_2O and one Cl atom from $ZrCl_3$
3. **HCl desorbs**

The H_2O complex is very stable!

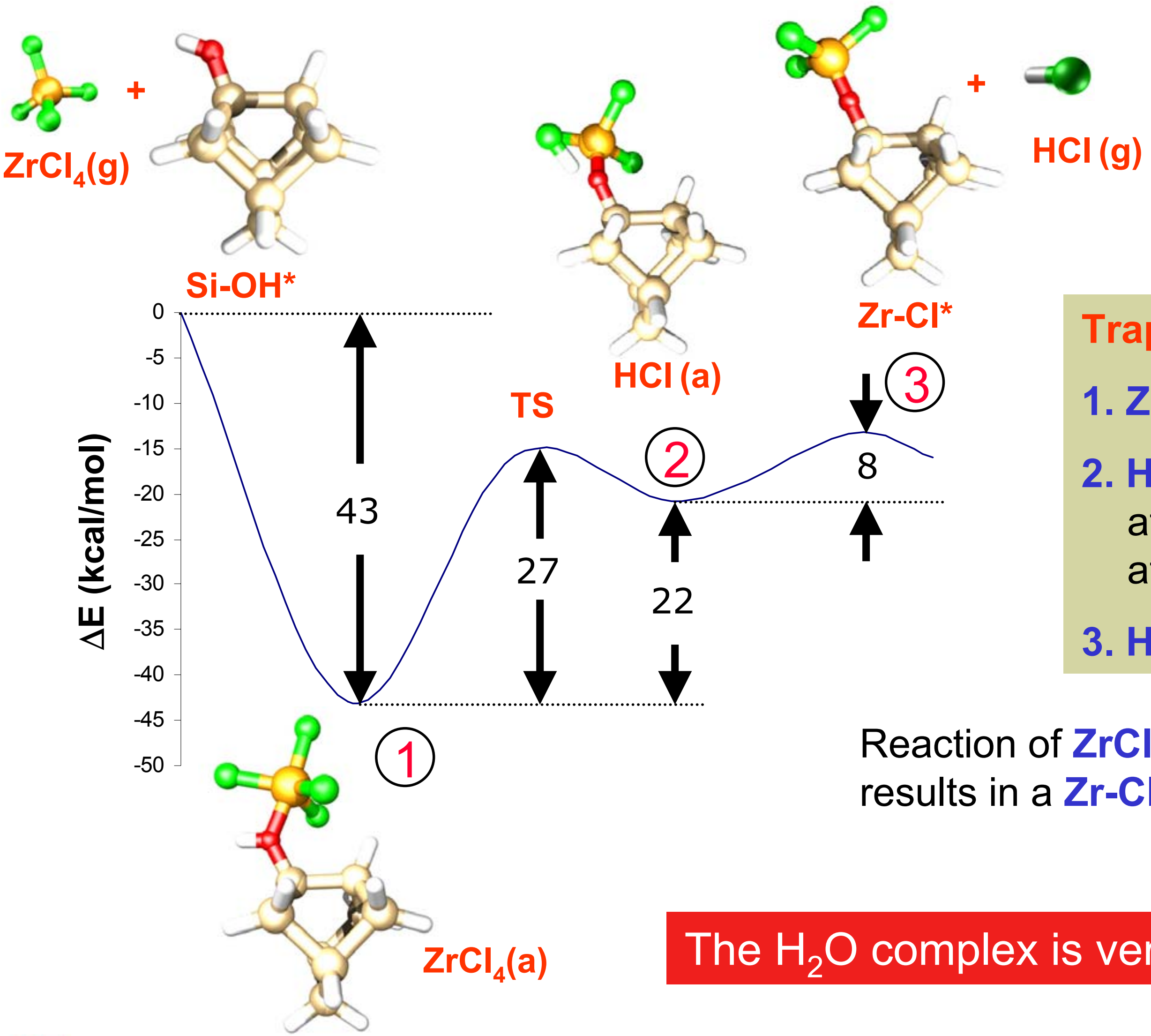
Reaction of H_2O with the Si-Cl* Surface Site



Direct dissociation reaction:

1. No stable complex formed
2. Reaction with **H_2O** with the **Si-Cl*** site results in a **Si-OH*** site in place of the **Si-Cl*** site

Reaction of $ZrCl_4$ with the Si-OH* Surface



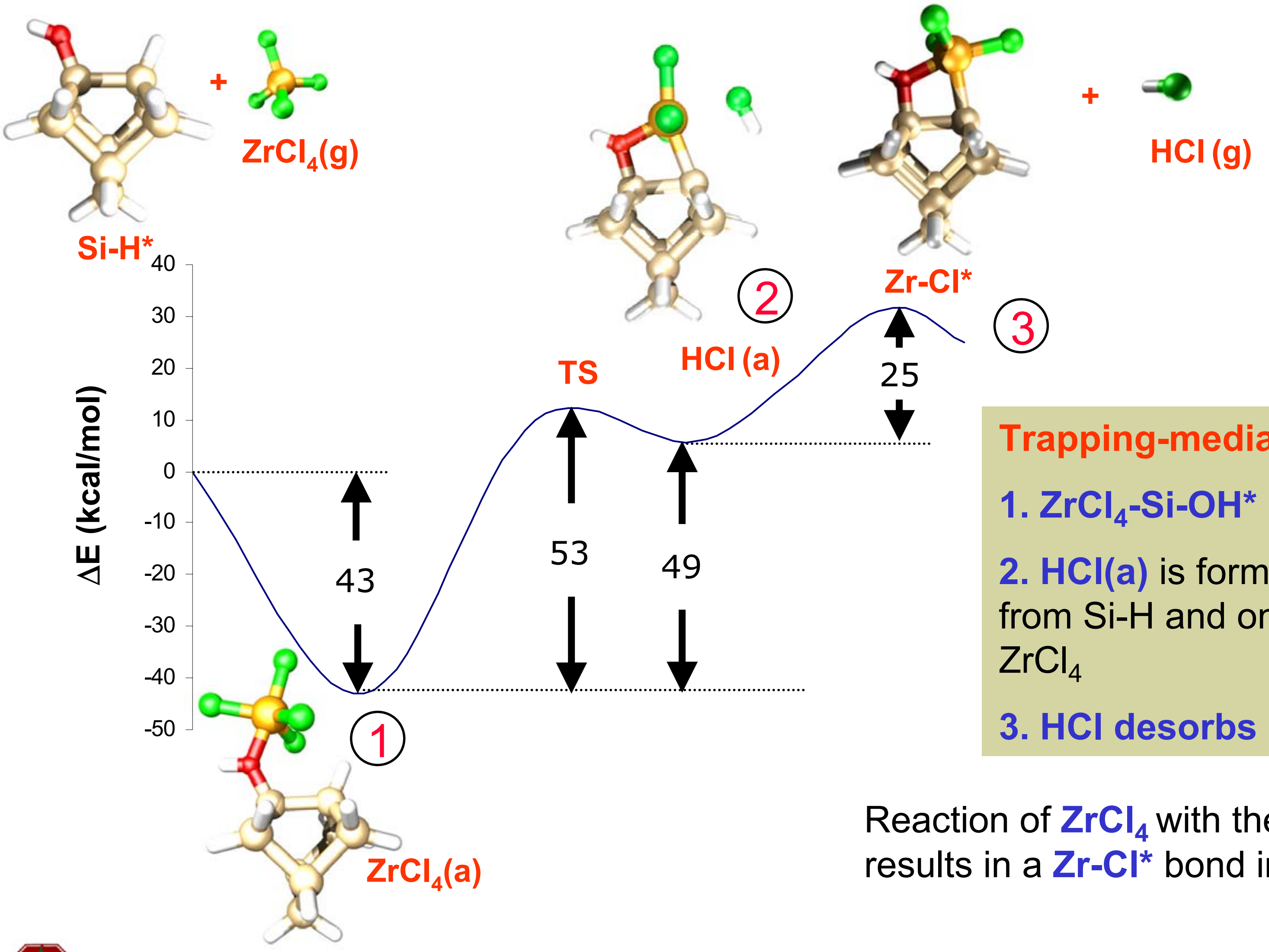
Trapping-mediated mechanism:

1. **$ZrCl_4$-Si-OH* complex** is formed
2. **HCl(a)** is formed from one H atom from Si-OH and one Cl atom from $ZrCl_4$
3. **HCl desorbs**

Reaction of **$ZrCl_4$** with the **Si-OH*** surface site results in a **Zr-Cl*** in place of **Si-OH***

The H_2O complex is very stable!

Reaction of $ZrCl_4$ with the Si-OH* Surface



Trapping-mediated mechanism:

1. **$ZrCl_4$-Si-OH* complex** is formed
2. **HCl(a)** is formed from one H atom from Si-H and one Cl atom from $ZrCl_4$
3. **HCl desorbs**

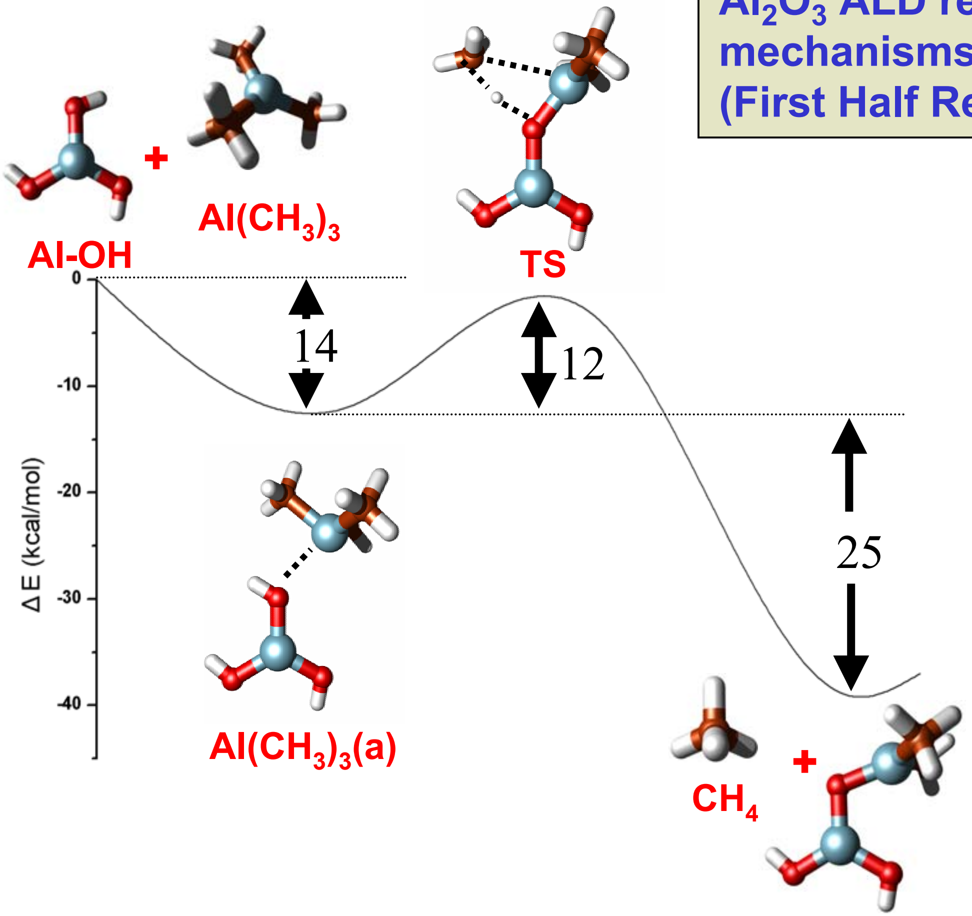
Reaction of **$ZrCl_4$** with the **Si-H*** surface site results in a **Zr-Cl*** bond in place of **Si-H***

Al_2O_3 ALD from TMA and Water

Mechanism of First Half Reaction

- TMA adsorbs molecularly on to Al-OH* surface site
- -CH_3 group from TMA reacts with H atom from surface –OH*
- Desorption of CH_4 and formation of -O-Al-$(CH_3)_2$*

Al_2O_3 ALD reaction mechanisms (First Half Reaction)

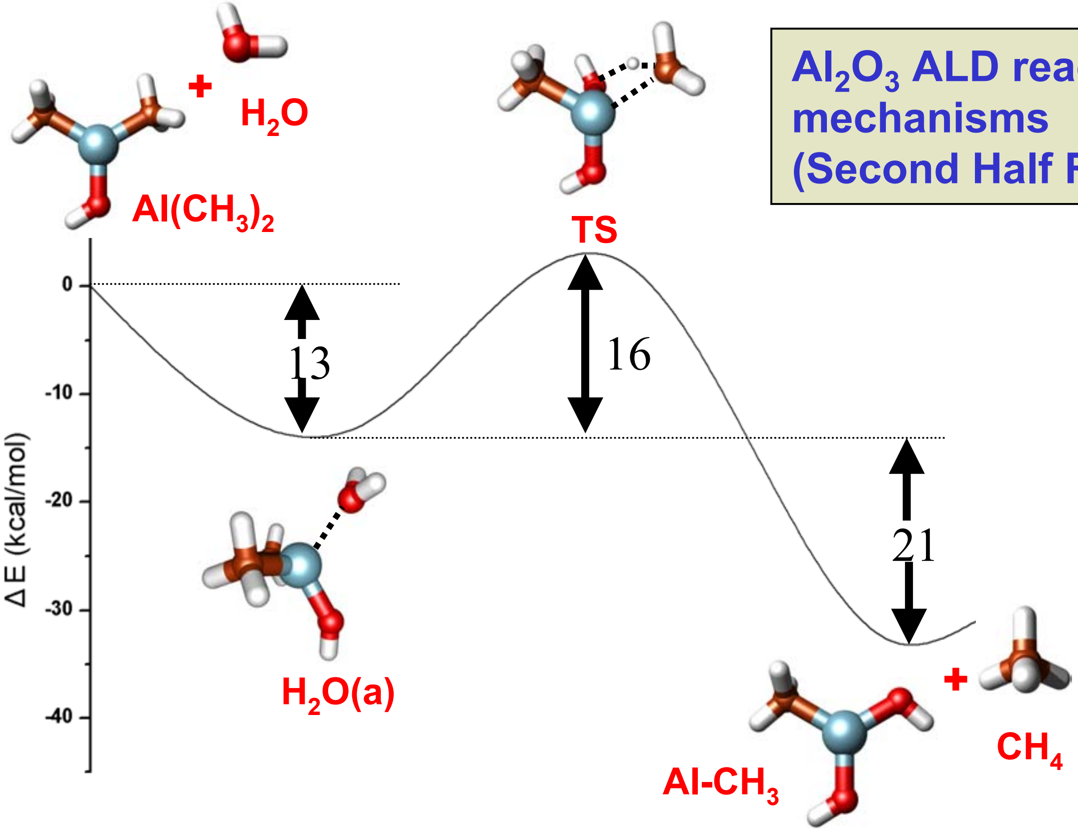


$Al\text{-}OH^* + Al(CH_3)_3 \rightarrow Al\text{-}O\text{-}Al\text{-}CH_3^* + CH_4$

Quantum Chemical Study of Al_2O_3 ALD

Mechanism of Second Half Reaction

- H_2O adsorbs molecularly on to Al-$(CH_3)_2$* surface site
- -CH_3 group from surface site reacts with H atom from H_2O
- Desorption of CH_4 and formation of Al-OH*



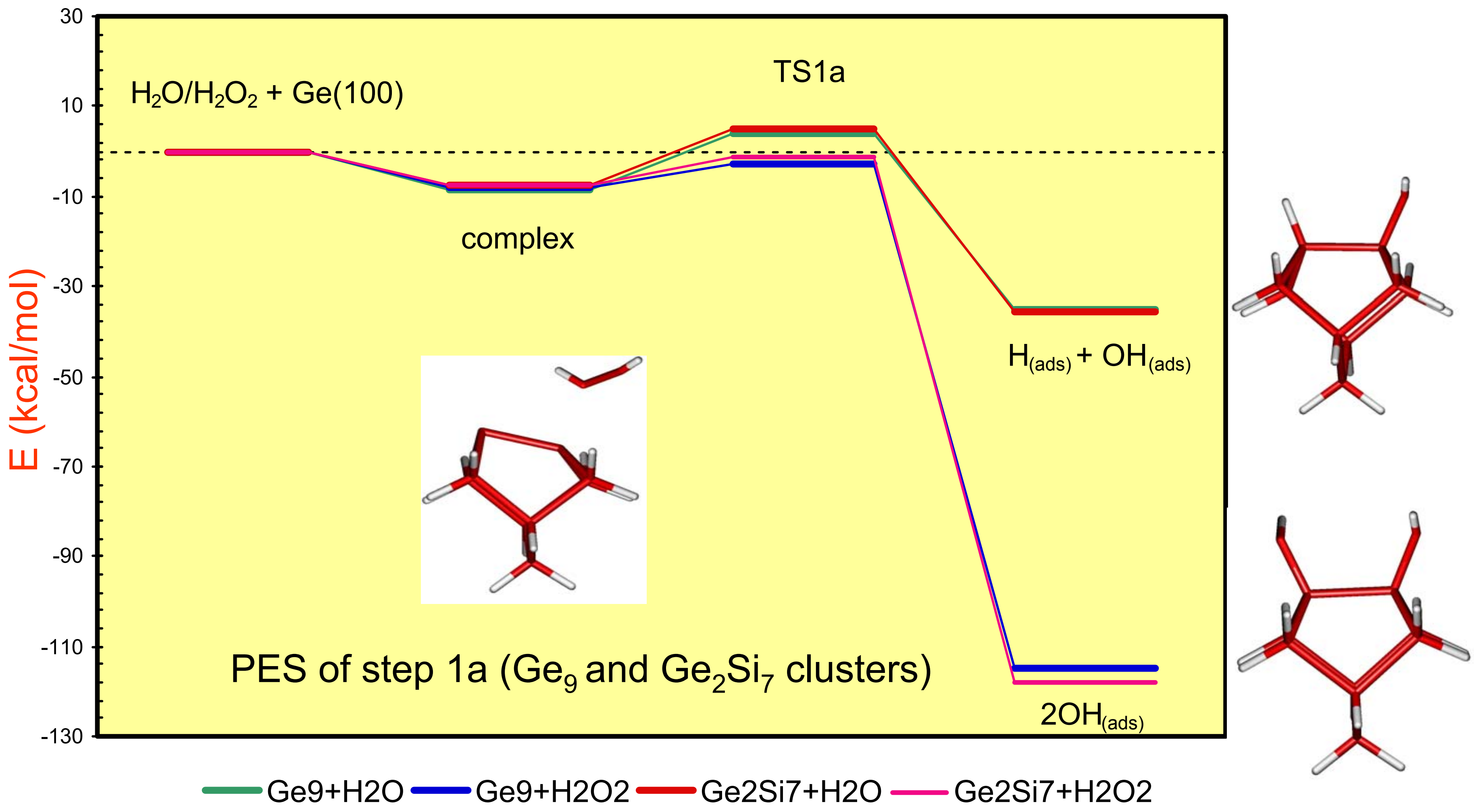
Al_2O_3 ALD reaction mechanisms (Second Half Reaction)

Al-CH_3*+H_2O→Al-OH*+CH_4

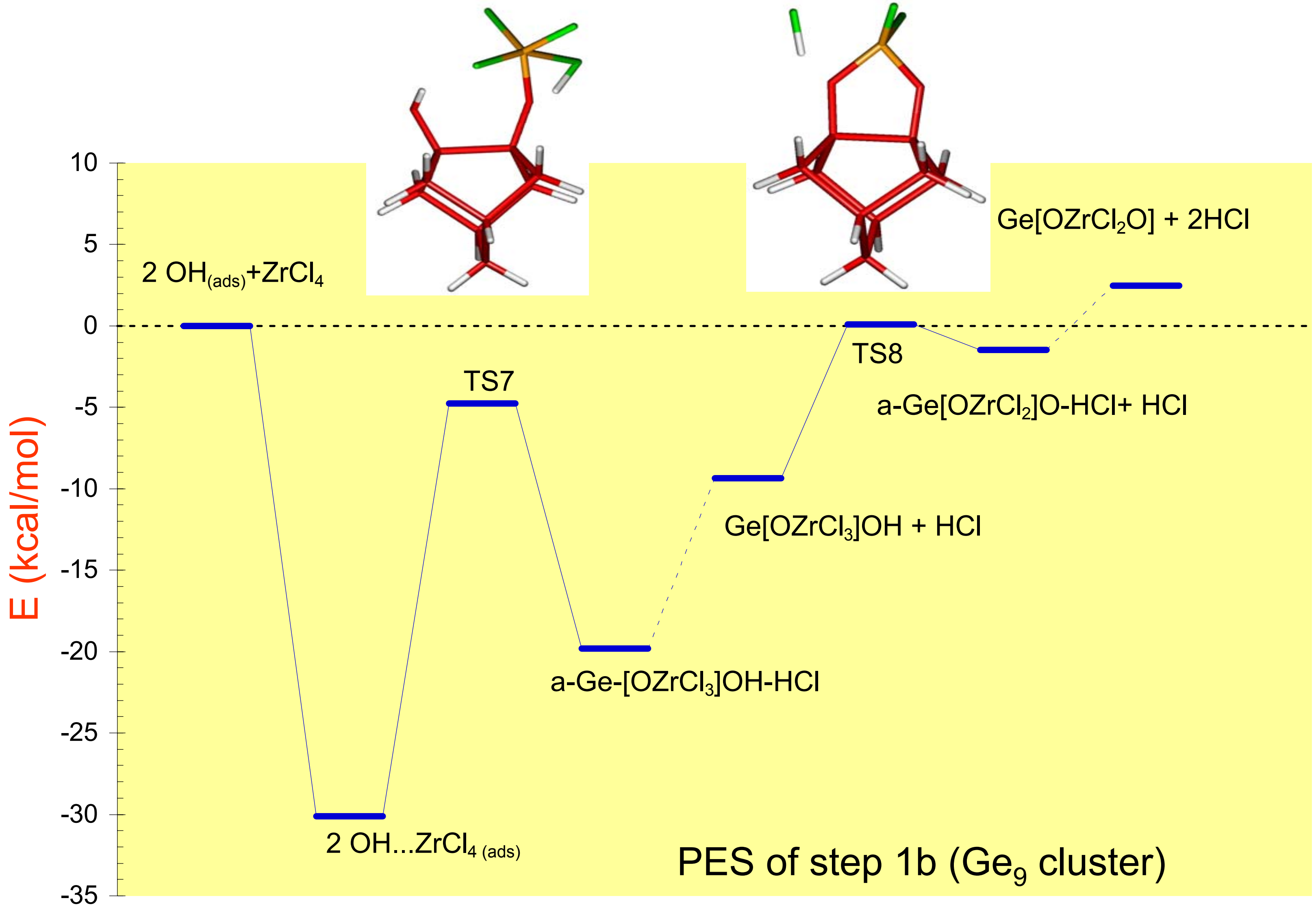
Advantages of Germanium

- Well understood Group IV material
- Narrower band gap which might allow Ge based transmitters and receivers in optical interconnects
- Higher mobility for both electrons and holes
- No interlayer oxide due to relative instability of GeO_2
- Less dependence of velocity saturation below 32nm node
- Significantly lower processing temperatures

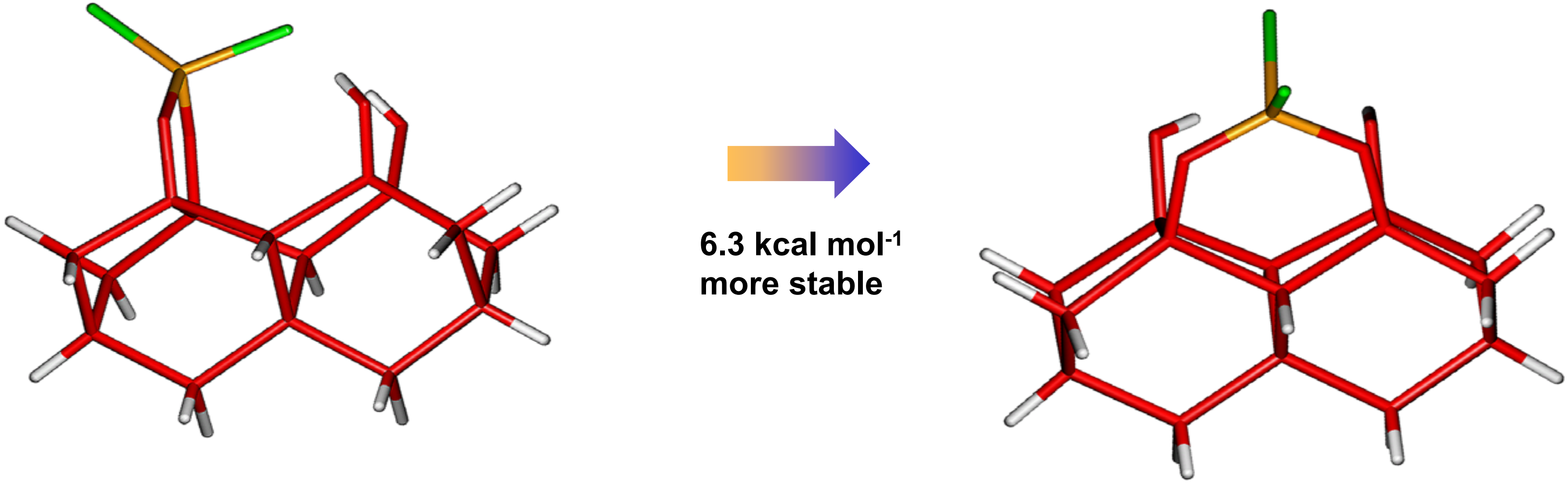
Dissociative Adsorption of H_2O/H_2O_2



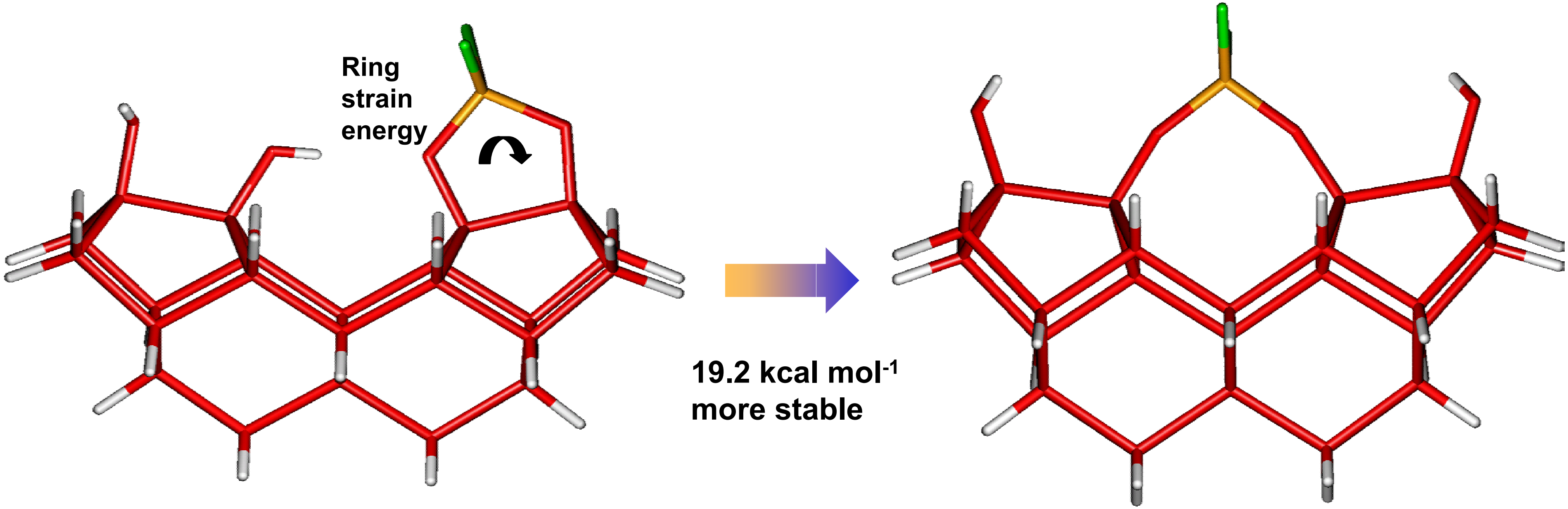
$ZrCl_4$ Initial Reaction on Ge-OH



Bridging Across the Trench



6.3 kcal mol^{-1}
more stable



19.2 kcal mol^{-1}
more stable

Summary

- Detailed mechanisms proposed for ZrO_2, HfO_2 and Al_2O_3 ALD reactions. Additional reactions (for example elimination of H_2O by condensation reactions) calculated or being studied.

- Calculations show that submonolayer coverage mostly due to desorption of precursor from the surface, NOT steric effects for ALD of high-K using chloride precursors.

- Al_2O_3 ALD using TMA should have higher growth rates (monolayers/cycle).

- Calculations indicate that the hydroxylation of Ge surfaces with H_2O_2 is kinetically more favorable.

- ALD with $ZrCl_4$ precursors is more favorable when the second ligand bond is formed across the trench.

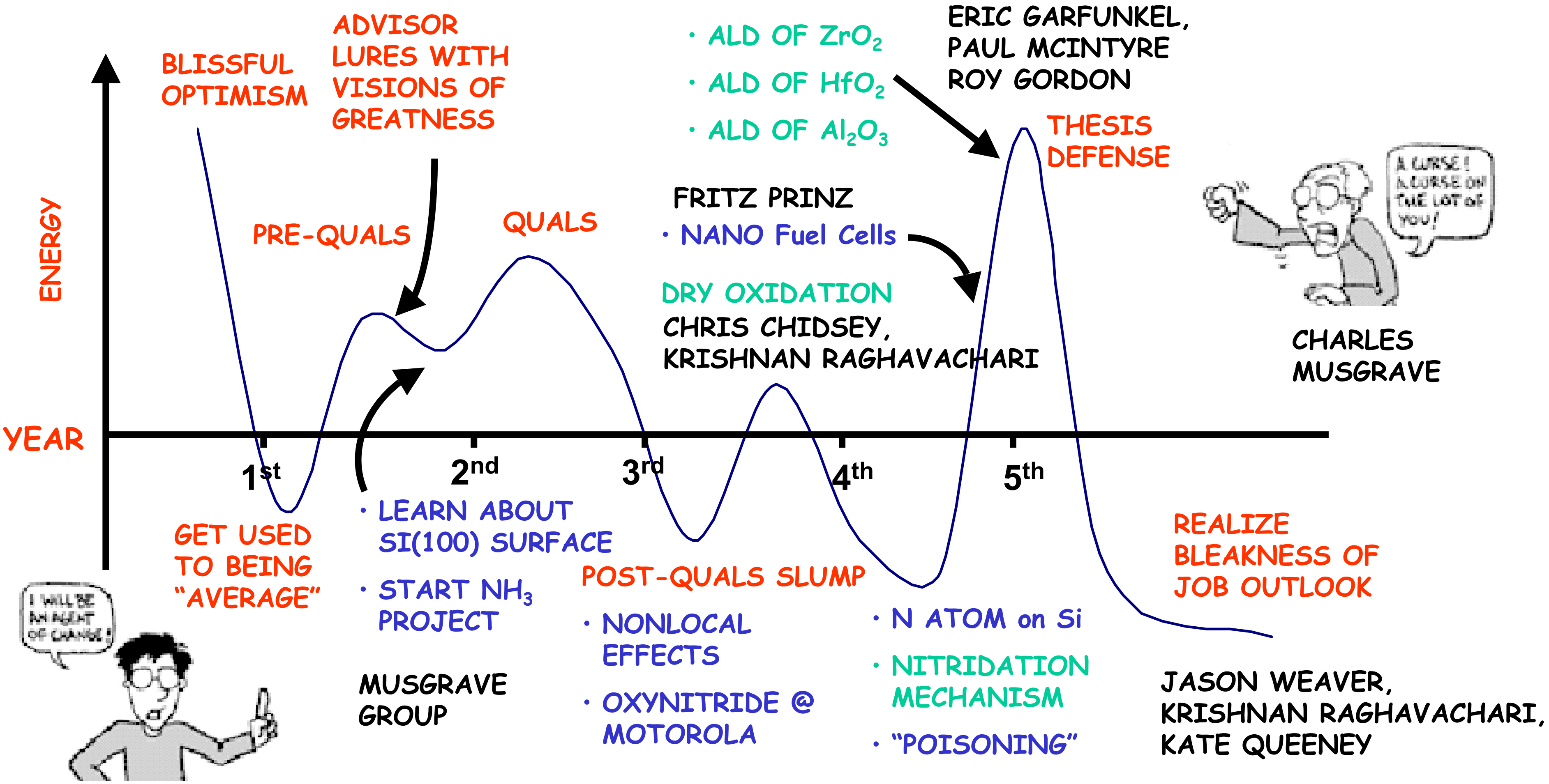
- Other precursors such as metal alkoxides, cyclopentadienyls or β-diketonates might result in faster deposition rates.

Acknowledgments:

A graduate student Potential Energy Surface

Yuniarto Widjaja

CHARLES POWELL FOUNDATION, MOTOROLA, STANFORD, DARPA, SRC MARCO MSD Center



BLISSFUL OPTIMISM

ADVISOR LURES WITH VISIONS OF GREATNESS

PRE-QUALS

QUALS

- ALD OF ZrO_2
- ALD OF HfO_2
- ALD OF Al_2O_3

ERIC GARFUNKEL,
PAUL MCINTYRE
ROY GORDON

THESIS DEFENSE

FRITZ PRINZ

- NANO Fuel Cells

DRY OXIDATION
CHRIS CHIDSEY,
KRISHNAN RAGHAVACHARI

CHARLES MUSGRAVE

GET USED TO BEING "AVERAGE"

- LEARN ABOUT SI(100) SURFACE
- START NH_3 PROJECT

MUSGRAVE GROUP

POST-QUALS SLUMP

- NONLOCAL EFFECTS
- OXYNITRIDE @ MOTOROLA

PETER VENTZEK,
VERNON COLE

- N ATOM on Si
- NITRIDATION MECHANISM
- "POISONING"

REALIZE BLEAKNESS OF JOB OUTLOOK

JASON WEAVER,
KRISHNAN RAGHAVACHARI,
KATE QUEENEY

Yuniarto Widjaja