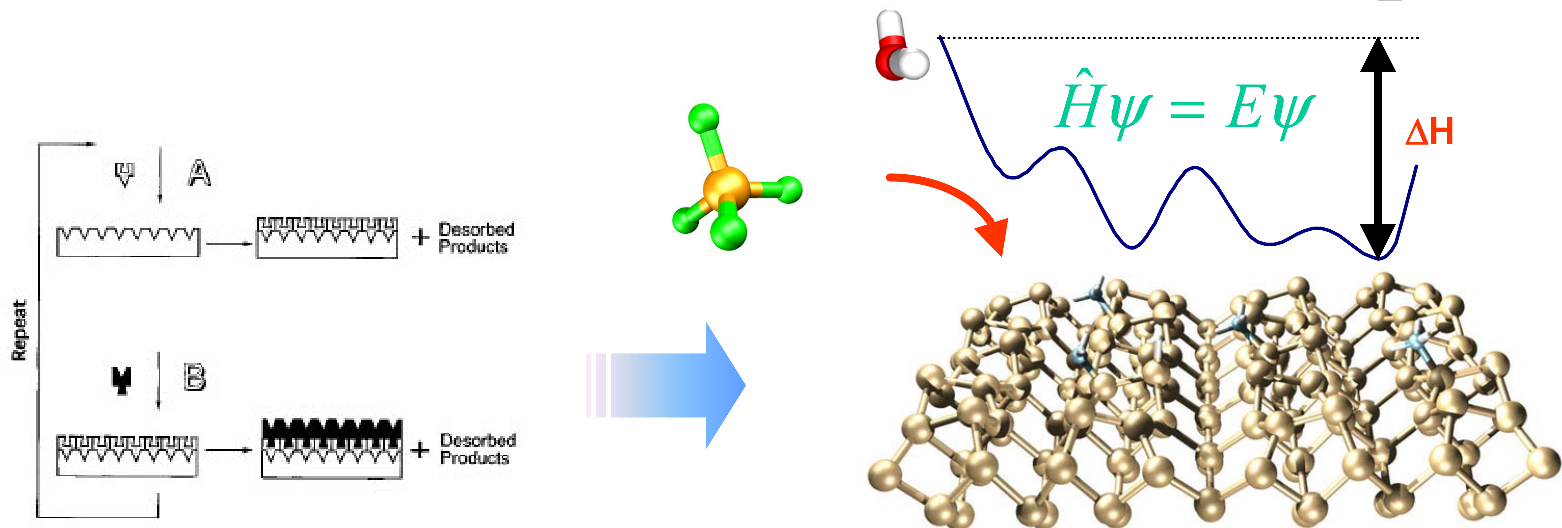
Quantum Chemistry Study of ZrO_2 ALD



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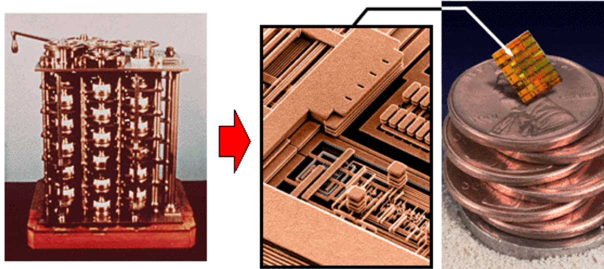
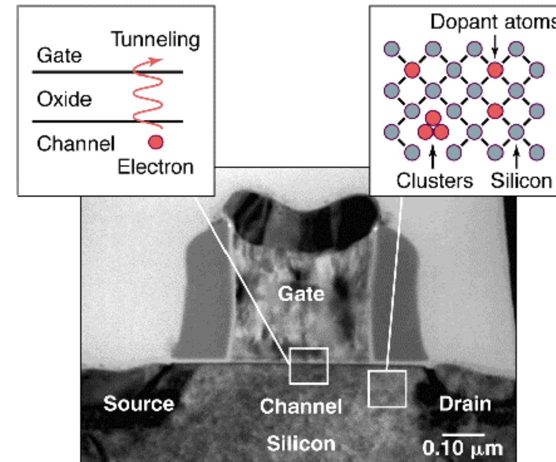
Introduction



An early computing machine built from mechanical gears and a state-of-the art IBM chip with 0.25 micron features. (Source: http://www.qubit.org)

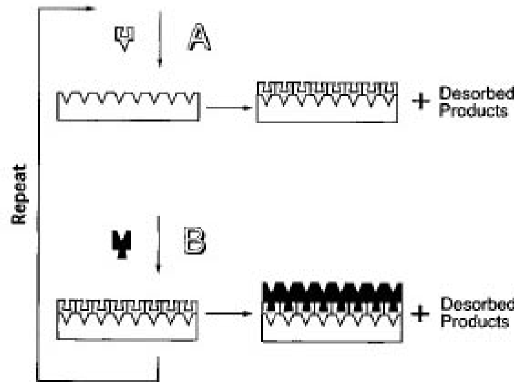


P.A. Packan, Science, 1999

- The scaling of metal-oxide-semiconductor (MOS) devices to sub-nanometer feature sizes requires **thin gate insulators**.
- **Leakage currents** caused by **electron tunneling** increases exponentially with decreasing dielectrics thickness.
- Using high-κ materials allows deposition of thick films with an effective thickness equivalent to thin SiO_2 films.

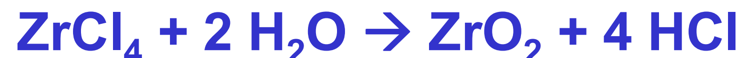
Atomic Layer Deposition

- Atomic Layer Deposition (ALD) occurs through a sequence of **self-limiting** surface reaction steps



Schematic representation of ALD using self-limiting surface chemistry and an AB binary reaction sequence (SM George, AW Ott, and JW Klaus, J. Phys. Chem, 1996)

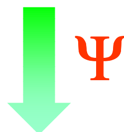
- ALD allows:
  - ➡ Atomic layer control because of the self-limiting nature of the surface reactions
  - ➡ Perfect conformality
- **Understanding of surface chemistry in ALD is very important!**
- Here, the ALD of ZrO_2 using $ZrCl_4$ and H_2O is investigated:



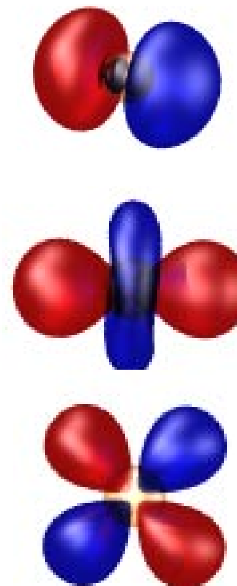
Quantum Chemistry

- Quantum chemistry:
  - ➡ first-principles description of molecular systems
  - ➡ allows accurate description of chemical bonds
  - ➡ allows detailed investigation of reaction mechanism

- Schrödinger equation: $\hat{H}\Psi = E\Psi$



Ψ

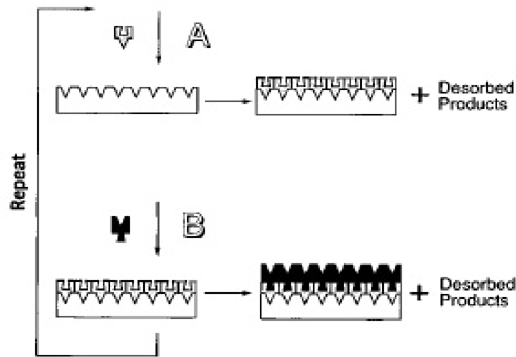


Energy

Force $\frac{\partial E}{\partial r}$

Frequency $\frac{\partial^2 E}{\partial r^2}$

Outline



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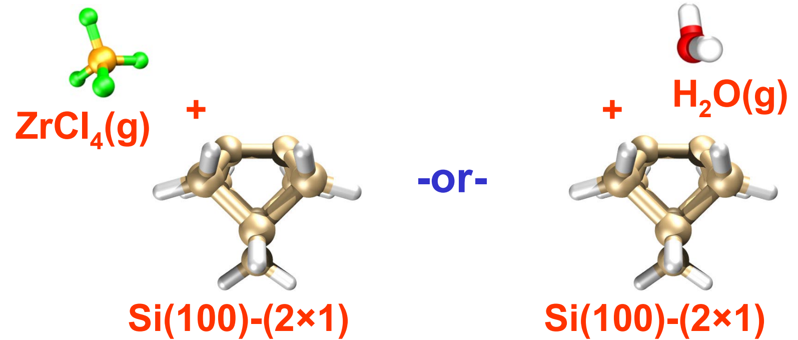

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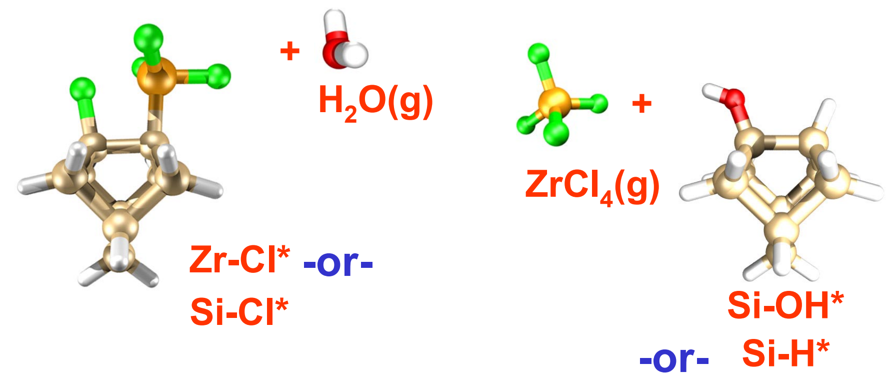

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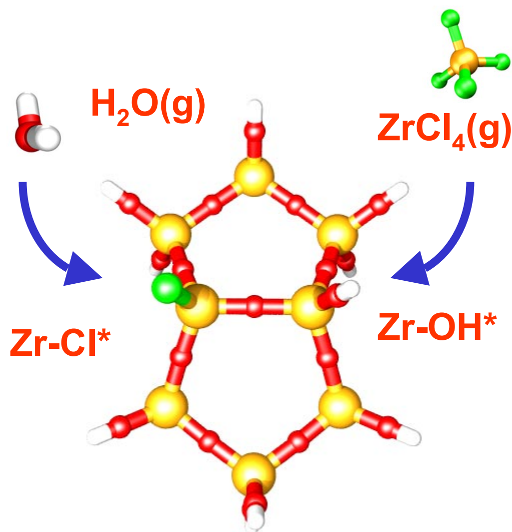
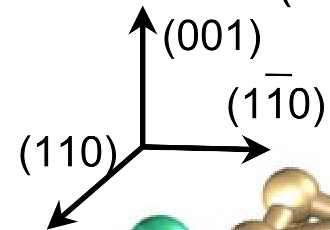
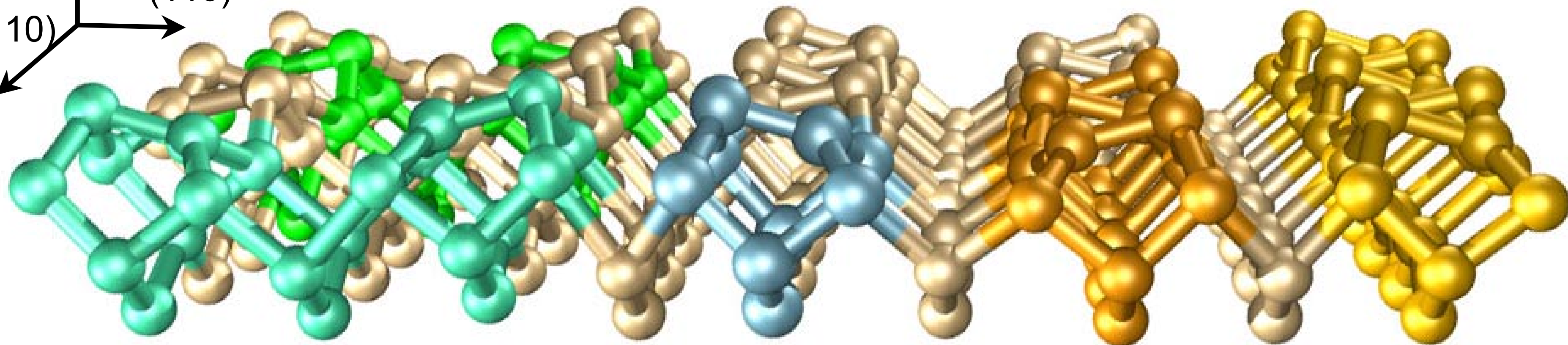


Surface Reaction Modeling

- Cluster approximations are used to model Si(100)-(2×1)
- Si(100)-(2×1) reconstruction:

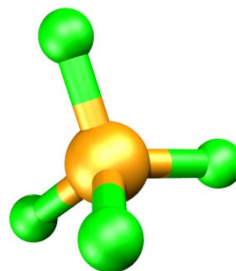




- Cluster models: 1-dimer (blue), 3-dimer (copper), 5-dimer (gold), V-trench, and Λ-trench (green).
- Hydrogen termination.

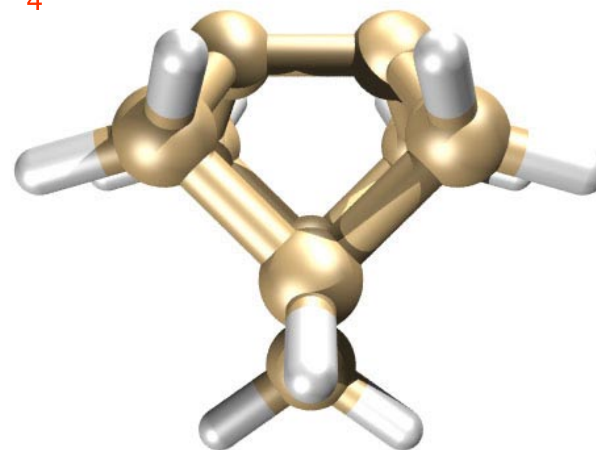
Calculational Details

- Method: KMLYP DFT
  - ➡ Good accuracy
  - ➡ Computational expense $\propto N^3$
- Basis Set: LANL2DZ ECP
  - ➡ Los Alamos LANL2 effective core potentials (ECP)
  - ➡ Valence double-ζ
- Constraints
  - ➡ Constraints are introduced by fixing the terminating H atoms in the ideal positions



$ZrCl_4$

H_2O

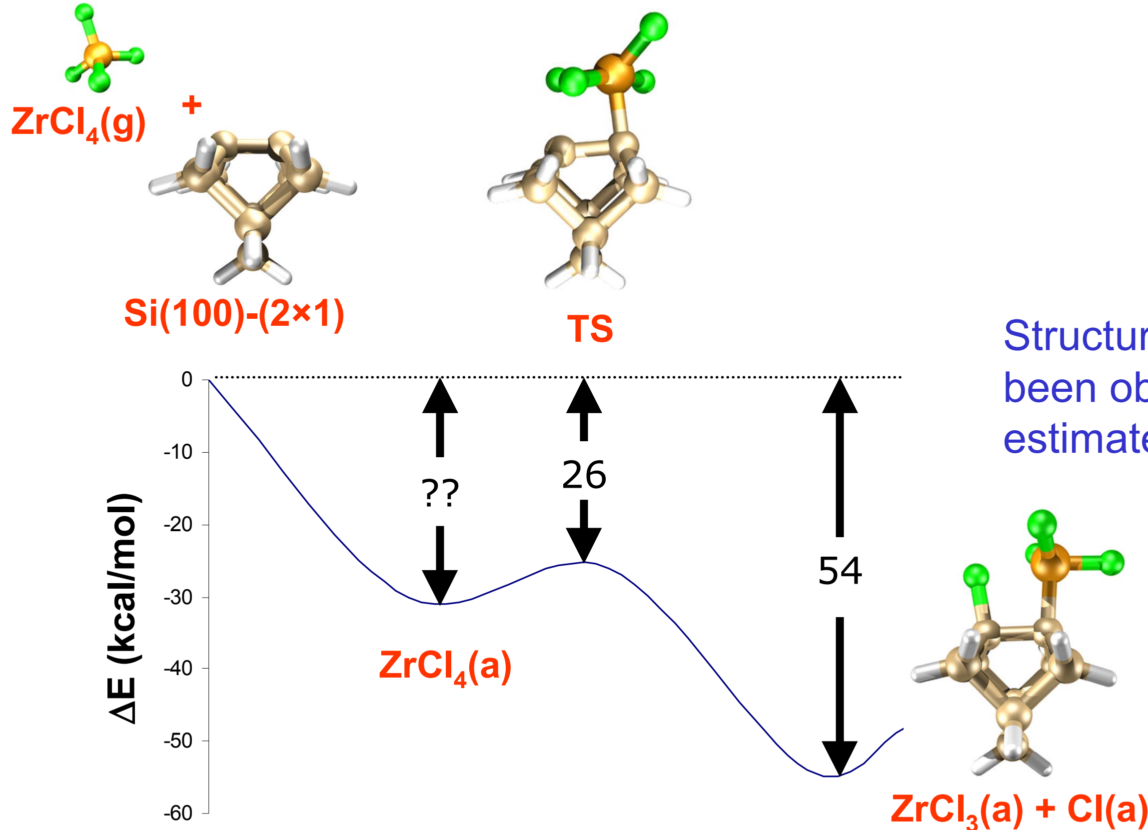


1-dimer cluster

Model for the Si(100)-(2×1) surface

Initial Adsorption and Decomposition

Reaction of $ZrCl_4$ on the Si(100)-(2×1) Surface

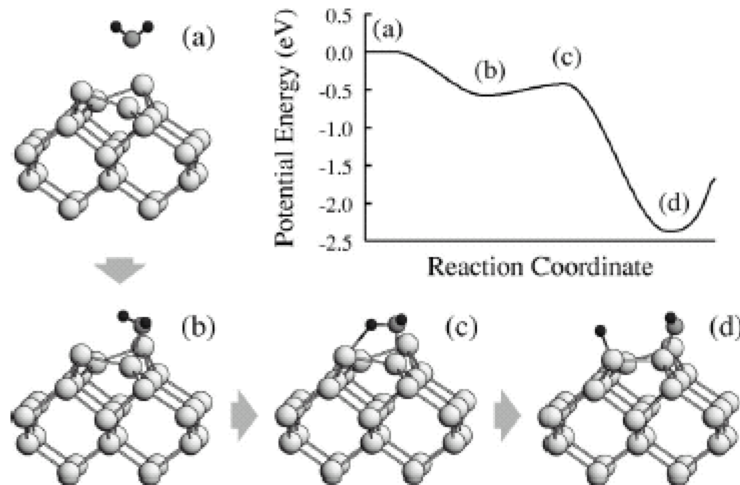


Structure of $ZrCl_4$(a) has not been obtained. However, ΔH_{ads} is estimated to be similar to E_{TS}

- $ZrCl_4$ dissociates into $ZrCl_3$(a) and Cl(a) on the Si(100)-(2×1) surface
- This results in **Zr-Cl*** and **Si-Cl*** surface sites

Initial Adsorption and Decomposition

Reaction of H_2O on the Si(100)-(2×1) Surface



Calculated energy profile for the dissociation process of water on Si(100) and atomic geometries at four representative points (JH Cho et al., PRB, 2000)

- H_2O decomposes to form OH(a) + H(a) on the Si(100)-(2×1) surface, resulting in a **Si-OH*** and **Si-H*** surface site.
- Subsequent H_2O reactions have also been investigate, resulting in **-OH** terminated surface. (JK Kang et al., J. Appl. Phys, submitted)

Subsequent ZrO_2 ALD Reactions

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!

Subsequent ZrO_2 ALD Reactions

Reaction of H_2O with the Si-Cl surface site*

$H_2O(g)$ +

Si-Cl*

TS

10

4

$HCl(g)$ +

Si-OH*

ΔE (kcal/mol)

12, 10, 8, 6, 4, 2, 0, -2, -4, -6

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

Subsequent ZrO_2 ALD Reactions

Reaction of $ZrCl_4$ with the Si-OH surface site*

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*** bonds in place of **Si-OH***

Subsequent ZrO_2 ALD Reactions

Reaction of $ZrCl_4$ with the Si-H surface site*

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*** bonds in place of **Si-H***

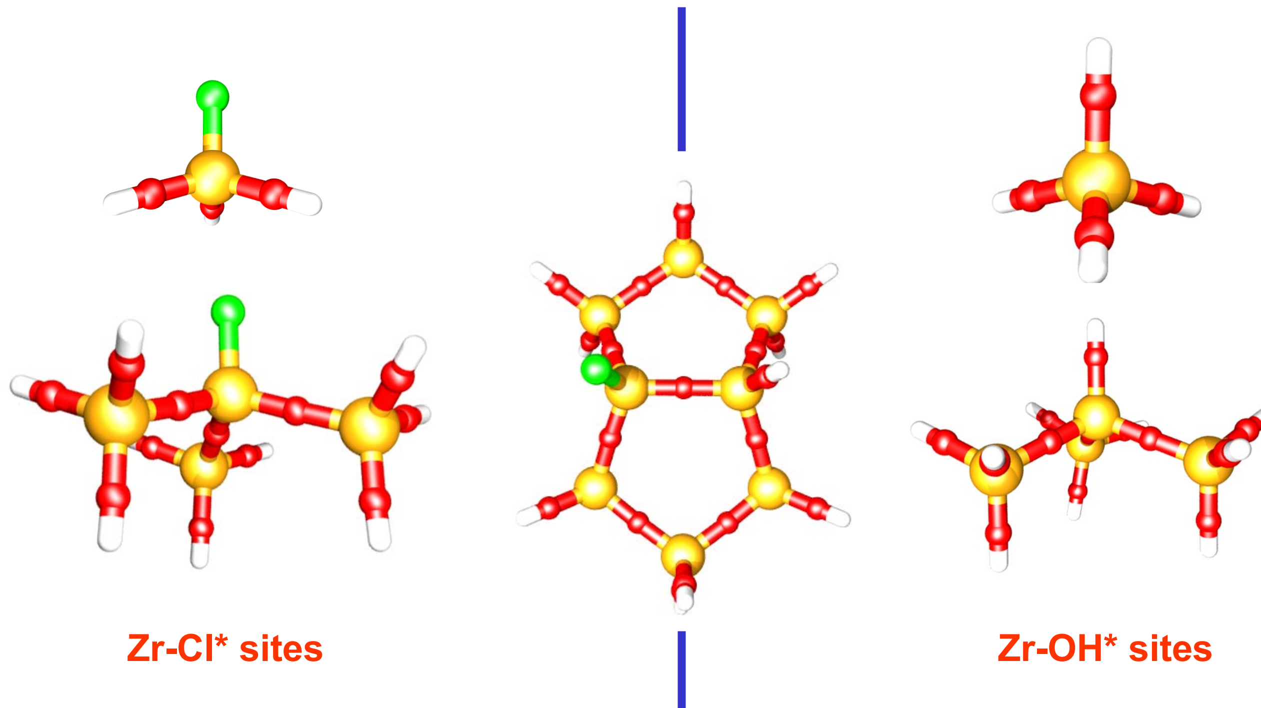
Summary on Initial Growth of ZrO_2

- First layer formation:
  - ➡ **$ZrCl_4$(g)** dissociates upon adsorption into **$ZrCl_3$(a) + Cl(a),** resulting in **Zr-Cl*** and **Si-Cl*** sites.
  - ➡ **H_2O(g)** forms **OH(a) + H(a)** upon dissociation, creating **Si-OH*** and **Si-H*** sites.
- Second layer formation:
  - ➡ Reactions on **Zr-Cl*, Si-OH*** and **Si-H*** follow **trapping-mediated mechanism**.
  - ➡ Reaction on **Si-H*** has a high barrier. This explains the slow growth on H-terminated surface.
- Interface structure:
  - ➡ **SiO_2-like** bonding is more stable than **silicide-like** bonding.

Subsequent ZrO_2 growth

Reactions on Zr-OH and Zr-Cl* sites*

- As-deposited films have been shown to be **amorphous**.
- Clusters are constructed not according to any specific crystal structures, but designed to investigate the **electronic effects** of neighboring groups.
- **Surface strain** is described by two 10-member Zr-O rings.



Subsequent ZrO_2 Growth

Reactions on Zr-OH site*

Zr-OH* + $ZrCl_4$(g)

HCl desorption TS (2)

Zr-O-$ZrCl_3$* (4) + HCl(g)

ΔH/ΔG (kcal/mol)

15, 10, 5, 0, -5, -10, -15, -20, -25, -30, -35

ΔG_{600}, ΔG_{298}, ΔH_0

(1) Zr-OH*-$ZrCl_4$ complex

(3) Zr-O-$ZrCl_3$*-HCl complex

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**

Subsequent ZrO_2 Growth

Reactions on Zr-Cl site*

Trapping-mediated pathway

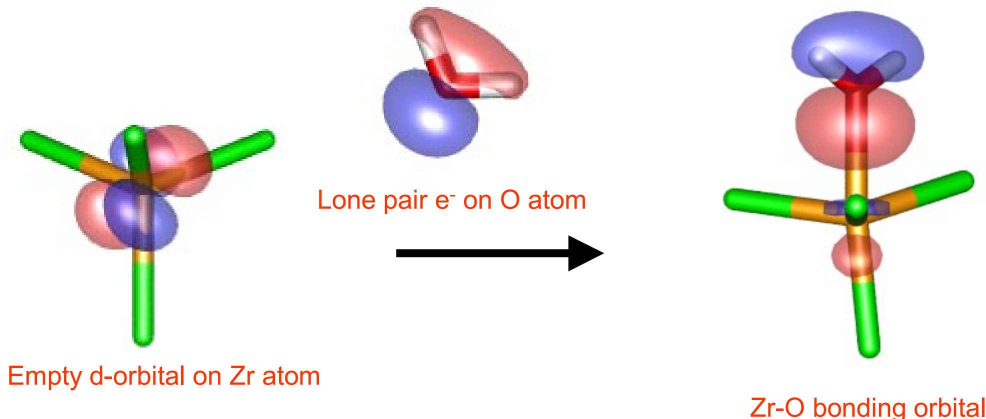
1. **Zr-Cl*-H_2O complex** is formed
2. HCl(a) formation transition state
3. **HCl(a)** is formed from one H atom from H_2O and one Cl atom from $ZrCl_3$
4. **HCl desorbs**

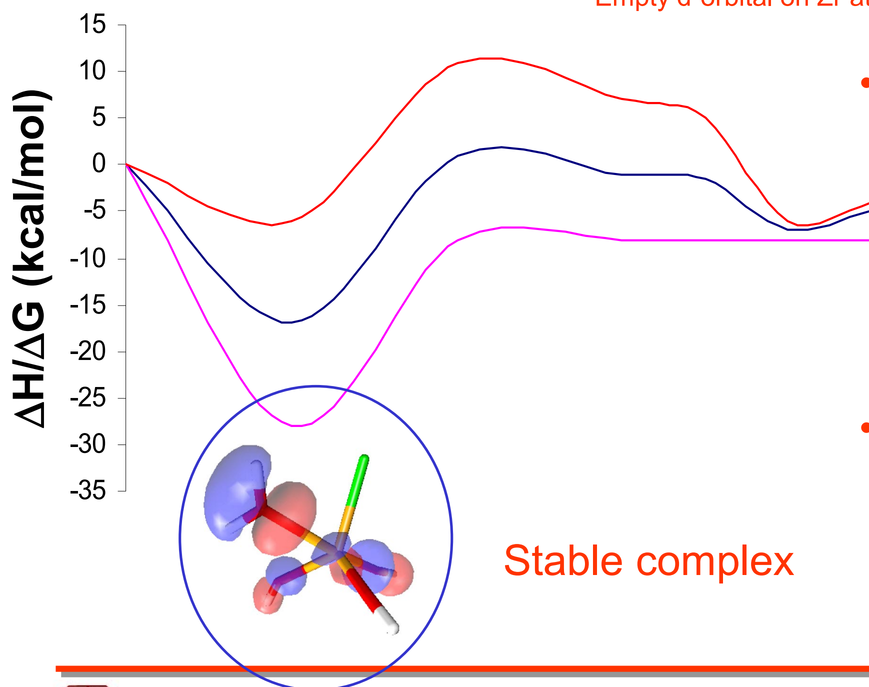
Potential Issues

Stable Complex formation

H_2O complex formation:

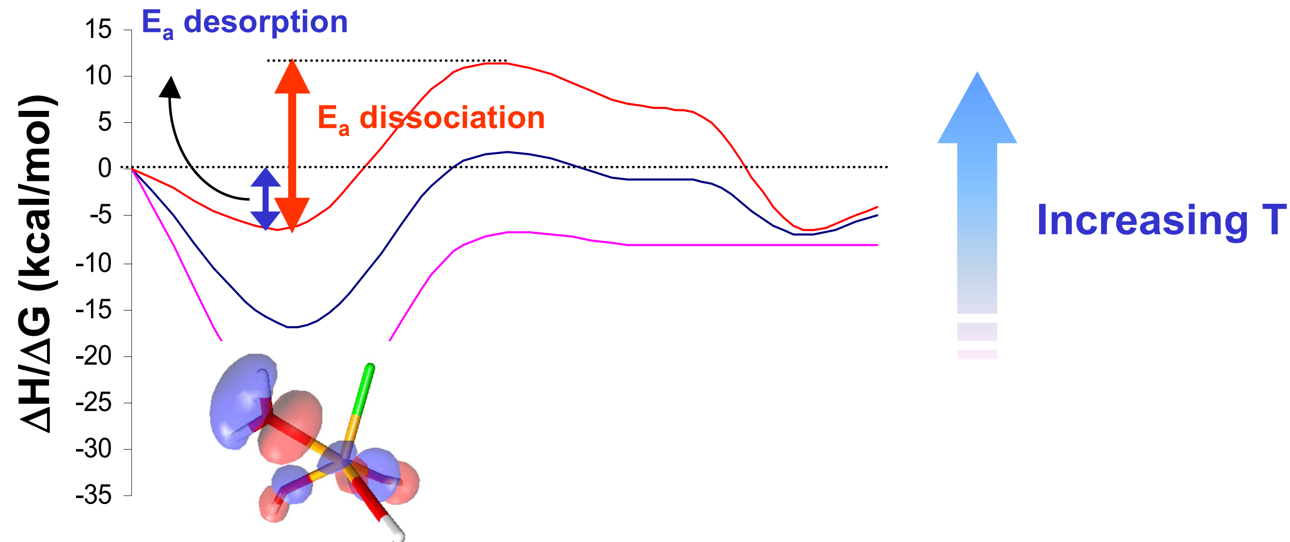
H_2O lone pair of electrons interacting with empty d-orbital on Zr atom





- Adsorbed complexes have lower energies than dissociated products, resulting from the strong interaction between H_2O lone pair electrons with empty d-orbital on Zr atom
  - ➡ prevents subsequent half-reaction cycles
- Solution: **raise temperature**
  - ➡ at high temperature, the adsorbed complexes become less favorable relative to the dissociated products

Potential Issues



- Raising the temperature brings up new issues:
  - ➡ Activation energy for the adsorbed complexes desorption becomes smaller than the activation energy for the dissociation reaction
  - ➡ More favorable for adsorbed complex to desorb and no reaction will occur on the surface or less than a monolayer coverage on the surface
    - – Solution: **increase the gaseous pressure** to minimize desorption of the adsorbed molecules from the surface
  - ➡ Low-thermal budget processing might be desired

Conclusion

- The ALD of ZrO_2 using $ZrCl_4$ and H_2O have been investigated. The binary reaction can be divided into two half-reactions:
    - ➡ Zr-OH* + $ZrCl_4$ → Zr-O-ZrCl* + HCl
    - ➡ Zr-Cl* + H_2O → Zr-OH* + HCl
- Detailed atomistic mechanisms of the deposition along with the energetics have been studied:
    - ➡ First layer on the clean Si(100)-(2×1) surface, resulting in four reaction sites: Zr-Cl*, Si-Cl*, Si-OH*, and Si-H.
    - ➡ Subsequent growth of ZrO_2 on both Zr-OH* and Zr-Cl* sites
- Understanding of the surface reactions reveals potential problems:
    - ➡ Stable complexes preventing further reactions
    - ➡ Raising the temperature results in more adsorbed complexes desorbing than further dissociate