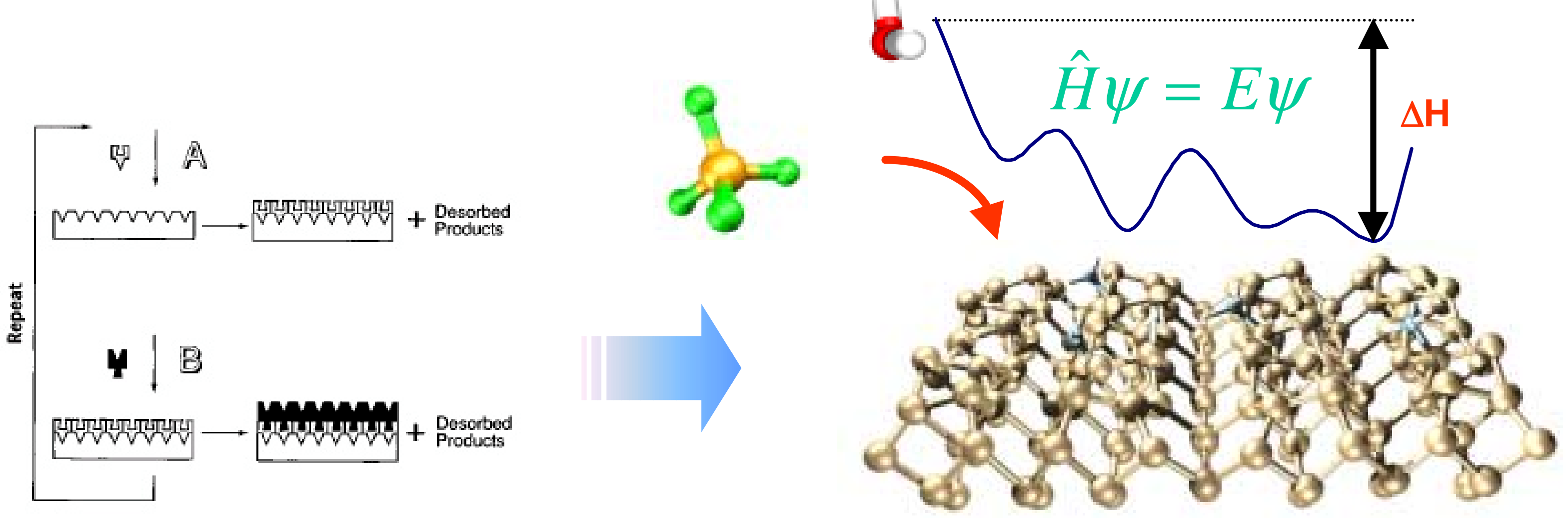
Simulations of Chemical Reactions for Semiconductor Processing



Jeung Ku Kang, Collin Mui, Yuniarto Widjaja, Stacey Bent

Department of Chemical Engineering

Charles B. Musgrave

Departments of Chemical Engineering & Materials Science and Engineering

Stanford University, Stanford, CA 94305

Motivation

- The chemistry of semiconductor processing is becoming increasingly complex.
- Many potential chemistries are relatively unexplored.
- Experiments for new processes are expensive.
- Process optimization is expensive.
- Many properties cannot be measured experimentally.

Quantum chemical simulations enables a much faster and more detailed exploration of new chemistries which are environmentally benign.

Quantum Chemistry

- Quantum chemistry:
  - first-principles description of molecular systems
  - allows accurate description of chemical bonds
  - allows detailed investigation of reaction mechanism
- Schrödinger equation: $\hat{H}\Psi = E\Psi$

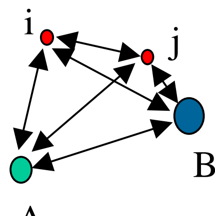
Ψ

Energy

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

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

Density Functional Theory



$$\hat{H} = -\sum_i \frac{\hbar^2}{2m}\nabla^2 - \sum_{iA} \frac{Z_A e^2}{r_{iA}} + \sum_{ij} \frac{e^2}{r_{ij}} + \sum_{AB} \frac{Z_A Z_B e^2}{r_{AB}}$$

$$\psi = \begin{vmatrix} \phi_1(1) & \phi_2(1) & \cdots & \phi_N(1) \\ \phi_1(2) & \phi_2(2) & \cdots & \phi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(N) & \phi_2(N) & \cdots & \phi_N(N) \end{vmatrix}$$

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

Ab Initio

$$\rho = \sum_i \phi_i \phi_i^*$$

$$E(\rho) = E_{KE}(\rho) + E_{NE}(\rho) + E_J(\rho) + E_X(\rho) + E_C(\rho)$$

DFT

Single-electron Hamiltonian Equation :

$$\frac{\partial E(\rho)}{\partial \rho} | \phi_i >= 0$$

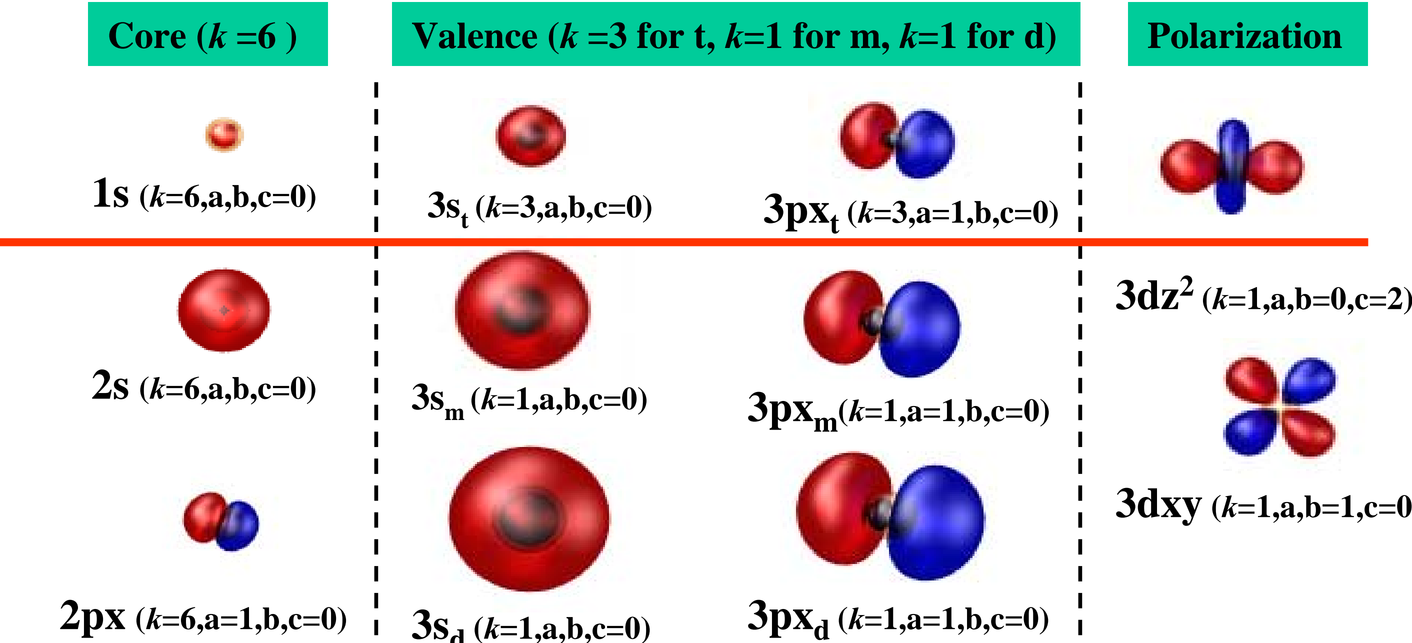
One-electron orbitals expanded in a basis of atomic-like basis functions

$$\phi_i = \sum_n c_n \varphi_n$$

Basis Set Expansions

Each orbital is a sum of basis functions

$$\phi_i = \sum_n c_n \varphi_n$$



Accuracy of Methods

	Barriers (74 chemical reactions)		ΔH (58 reactions)	
	AMD	MAD	AMD	MAD
B3LYP	3.5	15.6	3.0	20.7
G2	3.1	13.4	1.4	7.5
KMLYP	0.9	2.6	1.2	5.6
CBS-QCI/APNO	1.0	2.2		

J. K. Kang, and C. B. Musgrave, J. Chem. Phys., Dec. 22, 2001

Surface Reaction Modeling

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

(001)

$(1\bar{1}0)$

(110)

trench 1-dimer 3-dimer 5-dimer

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

Initial Adsorption of O_2

Trapping-mediated pathway

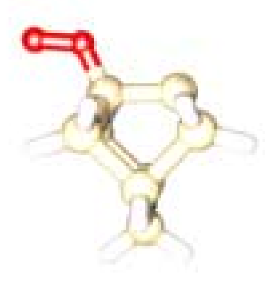
Trapping-mediated pathway

- O_2 initially adsorbs on the “up” Si dimer, forming O_2(a)
- O_2(a) then forms O_2(b) peroxide bridge structure

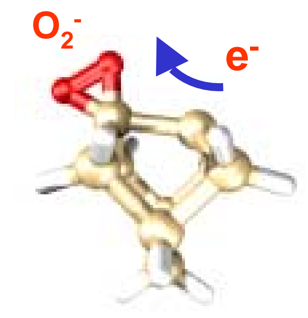
Molecular beam predicts a desorption barrier lower limit of 60 kcal/mol.

Source: Engstrom *et al.* (1991, 1992)

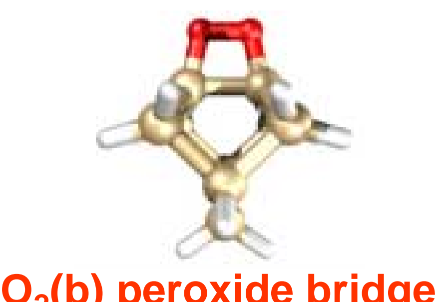
Chemisorbed Species



Peroxy radical



O_2(a) adsorbed state

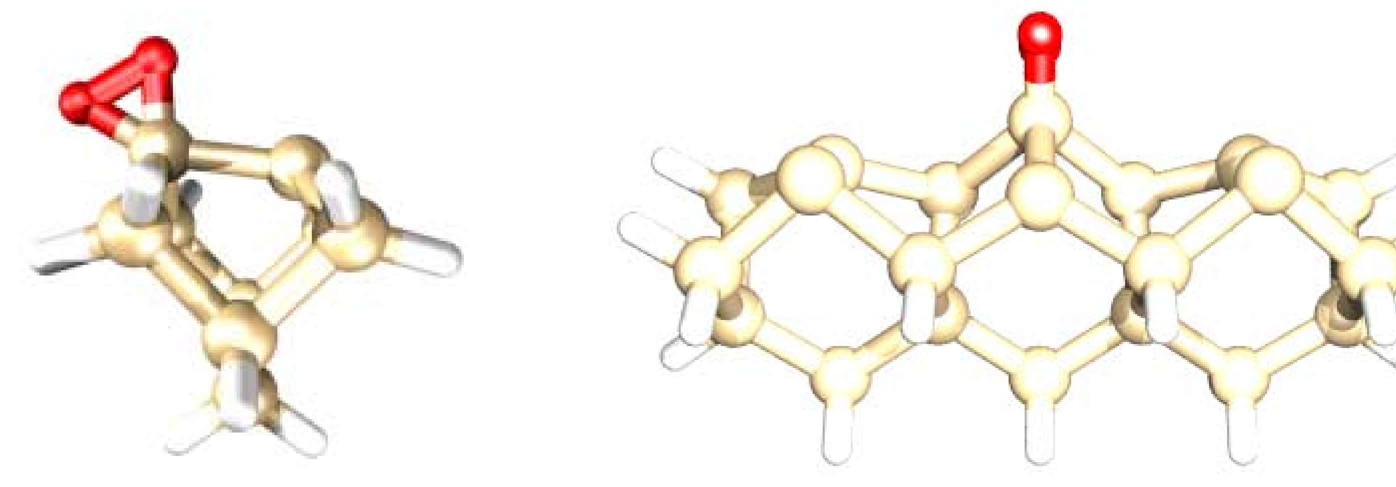


O_2(b) peroxide bridge

- Several species have been proposed as possible chemisorbed species:
  - peroxy radical (Hartree-Fock, Goddard *et al*., 1976)
  - peroxide bridge (UPS, Höfer *et al*., 1989)
  - O_2^- species (EELS, Silvestre and Shayegan, 1991)
- Peroxy radical is found to be unstable
- Both O_2^- and peroxide bridge are both calculated
  - O_2^- corresponds to O_2(a) adsorbed state

Nonlocal Effects

- Does charge transfer involved in formation of O_2(a) state extend to neighboring dimers?
- Adsorbed state is calculated using both **1-dimer** and **3-dimer** clusters.



E_{ads} = 35 kcal/mol **E_{ads} = 35 kcal/mol**

- The effects of O_2 adsorption on the Si(100)-(2×1) surface is localized.

Oxygen Insertion into Si(100)

- Oxygen insertion into Si-Si dimer vs. Oxygen insertion into Si-Si backbond

O(bb)-O(a)

0 kcal/mol

O(sb)-O(a)

-8 kcal/mol

More Stable

Oxygen Insertion into Si(100)

ΔE (kcal/mol)

0
-20
-40
-60
-80
-100
-120
-140
-160
-180

36
67
13
20

O_2(b) peroxide bridge

O(sb)-O(a)

O(sb)-O(bb)

Insertion mechanism

- Formation of one siloxane bridge and one siloxy radical, O(sb)-O(a) state
- Second insertion of oxygen into the backbond, O(sb)-O(bb) state.

Initial Oxidation Mechanism

ΔE (kcal/mol)

0
-20
-40
-60
-80
-100
-120
-140
-160
-180

35
10
33
36
67
13
20

O_2(a) adsorbed state

O_2(b) peroxide bridge

O(sb)-O(a)

O(sb)-O(bb)

Alternative Reaction Pathway

Direct Insertion into Si-Si backbond

-or-

ΔE (kcal/mol)
0
-20
-40
-60
-80
-100
-120
-140

??

34

4

122

Low reaction barrier leading to insertion into Si-Si backbond.

Mechanism NH_3 on Si(100)-(2×1)

ΔE (kcal/mol)

20
10
0
-10
-20
-30
-40
-50
-60
-70

26
20
51
55
28
38
57

NH_3(a)

NH_2(a) + H(a)

1
2
3
4

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).

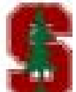
- Insertion barrier is higher than desorption barrier.
- TPD Spectra (Chen *et al.*, 1992)
  - ➡ 73% of NH_2(a) species will recombine with H(a)

Atomic N Insertion

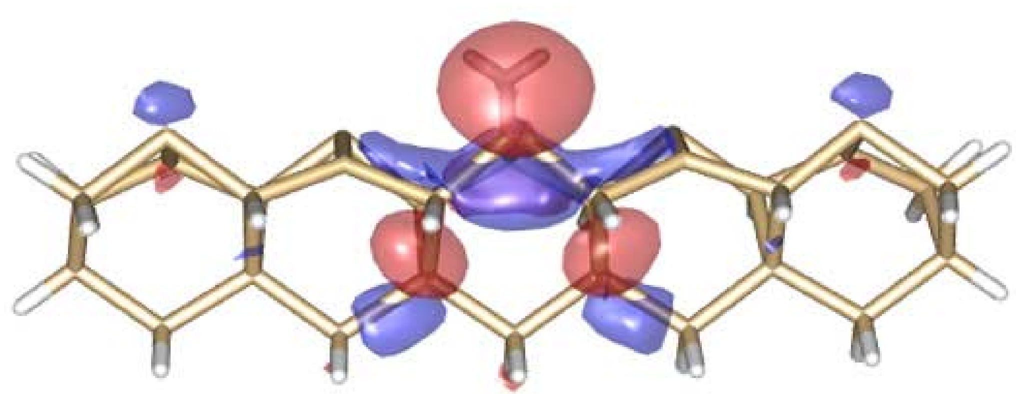
ΔE (kcal/mol)

0
-20
-40
-60
-80
-100
-120

60
30
32
35
3
6
6

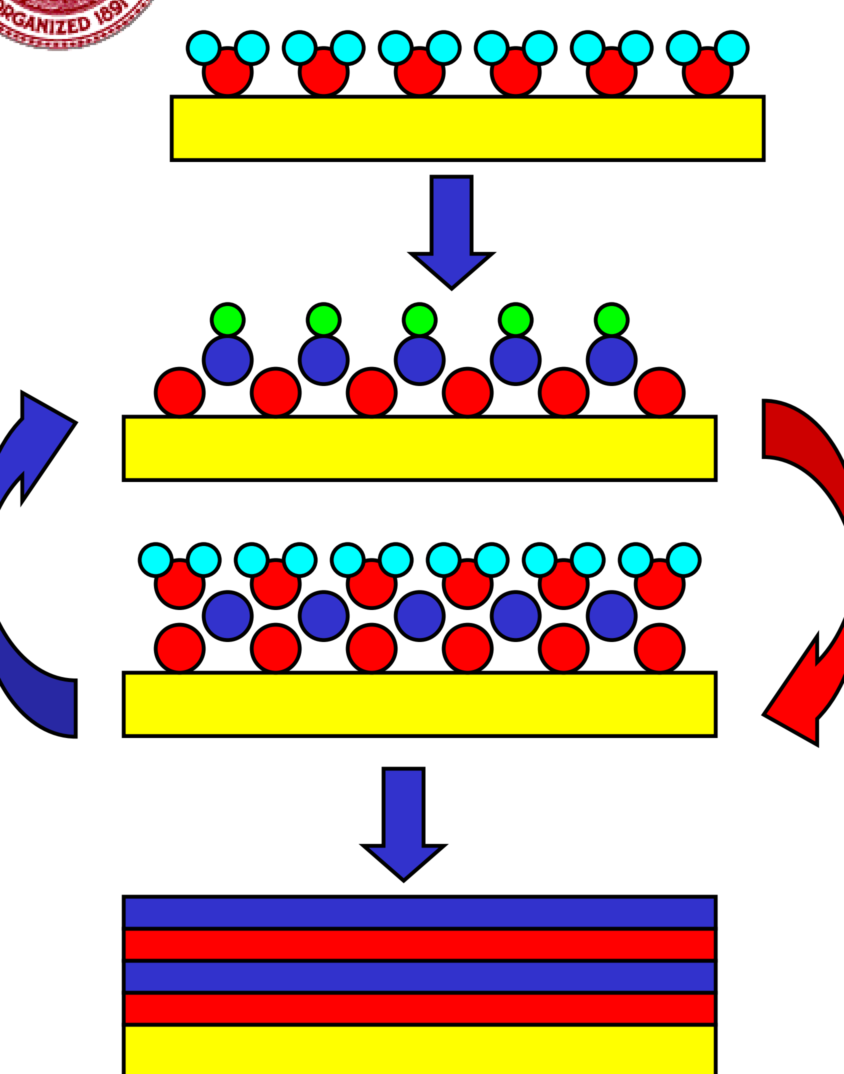


Nonlocal Effects



- Electron transfer from NH_3(g) to the Si(100) surface is delocalized to the neighboring dimers along the same row, on the same side.

Atomic Layer Deposition (ALD)



Advantages of ALD

- Accurate and simple thickness control
- Excellent conformality and reproducibility
- Atomic level control of material composition
- High quality materials
- Possibility for interface modification
- No gas phase reactions
- Wide processing temperature window
- Deposition of multilayer structures

Applications of ALD

- Electroluminescent display phosphors
- High-κ dielectrics for microelectronics
- Diffusion barriers for interconnects
- Transparent conductors
- Corrosion protection

Atomic Layer Deposition of SiO_2

Binary Reaction Sequence

Hydroxylation of bare silicon surface by water

$SiCl_4$ Half-Reaction

H_2O Half-Reaction

Reaction between $SiCl_4$ and adsorbed OH groups

Reaction between H_2O and adsorbed Cl groups

H_2O molecules

Each cycle results in one monolayer growth of SiO_2

Hydroxylation : Propsed Mechanisms

0.0

-12.5

-6.0

-62.7

25.5

-8.5

-4.6

-70.1

Active Pathway

-62.7

-29.4

-70.1

$SiCl_4$ Half-Reaction

0.0

15.8

-16.6

8.3

-10.7

Active Pathway

-16.6

6.0
(22.6)

Exp: 22 kcal/mol

-22.1

Catalytic Effect of NH_3 on $SiCl_4$ Half-Reaction

22.6

10.7

0.0

Exp:
10.2 kcal/mol

-7.5 (623 cm^{-1})

NH_3 simultaneously accepts one of H from a surface OH group and donates one of H to Cl atom of adsorbed $SiCl_3$(a)

Experimental Si-Cl Stretching : 625 cm^{-1}

H_2O Half-Reaction

0.0

19.1

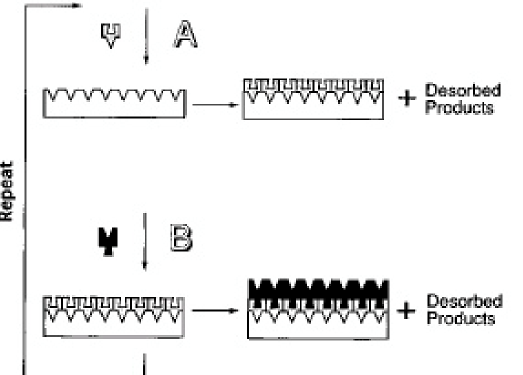
-4.8

6.9

-7.5

ZrO2 Atomic Layer Deposition

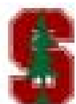
- Atomic Layer Deposition (ALD) occurs through a sequence of **self-limiting** surface reaction steps



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)

- Here, the ALD of ZrO_2 using $ZrCl_4$ and H_2O is investigated:

$$ZrCl_4 + 2\ H_2O \rightarrow ZrO_2 + 4\ HCl$$



ZrO2 ALD Surface Reactions

Subsequent ZrO_2 ALD Reactions

Reaction of H_2O with the Zr-Cl* surface site

+ H_2O(g)

Zr-Cl*

TS

HCl(g) +

Zr-OH*

ΔE (kcal/mol)

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

31

32

2

7

3

2 HCl(a)

1 H_2O(a)

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

TS

$H_2O(g)$ +

Si-Cl*

ΔE (kcal/mol)

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

10

4

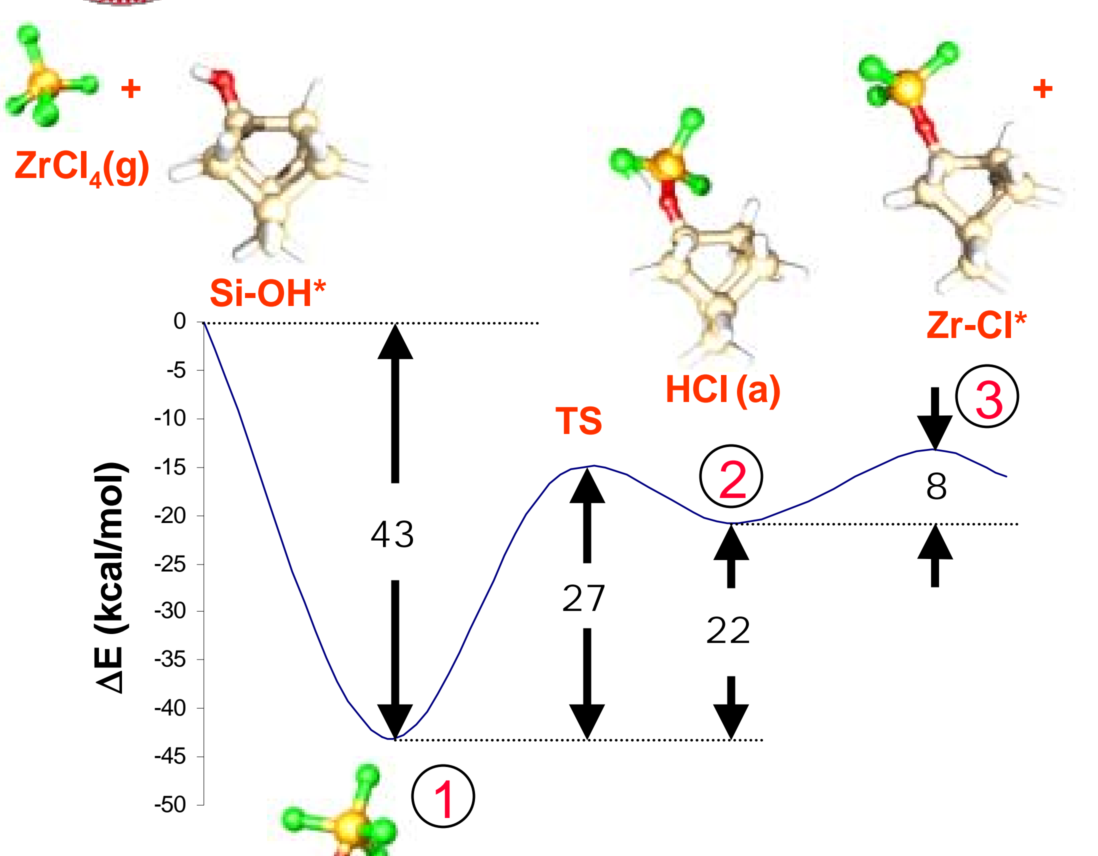
HCl(g) +

Si-OH*

- **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

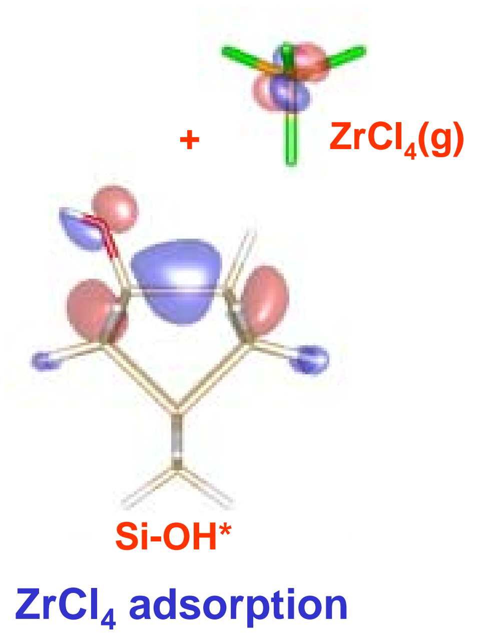


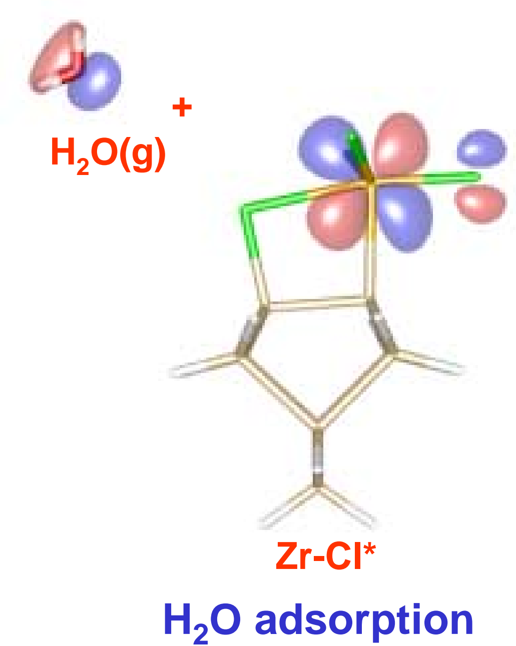
Trapping-mediated mechanism:

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***

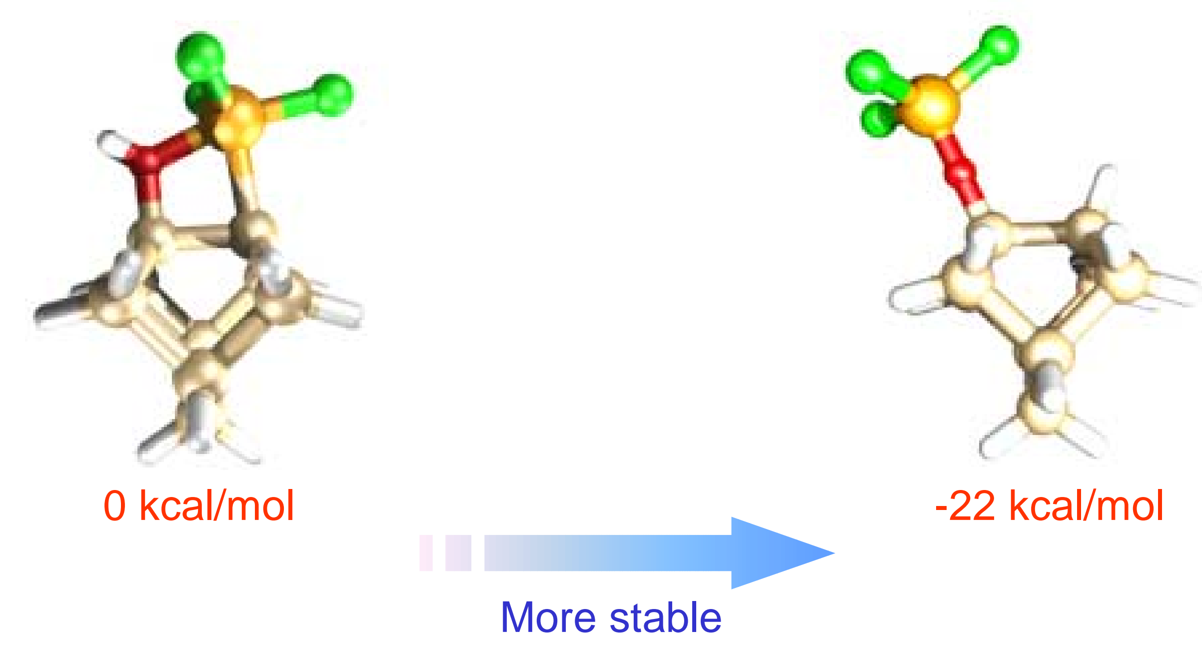
Zr-O Complexes





- Stable intermediates formed through the interaction between **an oxygen lone pair** with **an empty d-orbital of Zr atom**.
- **No complexes** formed between **Si** and **O** atoms since Si does not have low-lying empty orbitals.

Thermodynamics of Interface Structures



- **SiO_2-like** bonding is more stable than **silicide-like** bonding.
- This agrees with periodic slab calculations by Kawamoto *et al.*(IEEE Trans. Dev. Lett., 2001) that shows the SiO_2-like bonding is more stable than silicide-like bonding.

Subsequent ZrO_2 Growth

Reactions on Zr-OH* site

Zr-OH* + $ZrCl_4$(g)

HCl desorption TS

Zr-O-$ZrCl_3$* + 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

2 HCl desorption TS

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

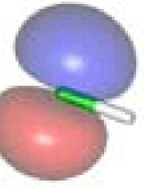
4 Zr-O-$ZrCl_3$*

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

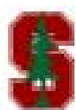
1. **Zr-Cl*-H_2O complex** is formed
2. HCl(a) formation transition state
3. **HCl(a)** is formed from one H atom from H_2O and one Cl atom from $ZrCl_3$
4. **HCl desorbs**

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:
  - ➡ $Zr\text{-}OH^* + ZrCl_4 \rightarrow Zr\text{-}O\text{-}ZrCl^* + HCl$
  - ➡ $Zr\text{-}Cl^* + H_2O \rightarrow Zr\text{-}OH^* + HCl$

- 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



Surface Modification for Selective ALD

Protected oxide

Modified Si Surface

ALD High-κ Dielectric

SiO_2 Si-H

OH OH OH OH H H H H

$RSiCl_3$

Protected SiO_2

R R R

Unreacted Si-H

O O O O H H H H

Cl_2

Protected SiO_2

R R R

Activated Si-Cl

O O O O Cl Cl Cl Cl

ALD Surface Chemistry of SiO_2

$SiCl_4$

Transition State

Cl-Termination

HCl

Surface Si-OH

E_A = 21.9 kcal/mol

ΔE = -7.8 kcal/mol

How to make use of ALD chemistry for surface passivation?

Protection of Surface Si-OH Groups

$SiCl(CH_3)_3$

Transition State

Protected Surface

HCl

Si-OH

E_A = 29.7 kcal/mol

ΔE = -0.4 kcal/mol

$SiCl_3CH_3$

Transition State

Protected Surface

HCl

Si-OH

E_A = 22.5 kcal/mol

ΔE = -6.4 kcal/mol

Cl substitution reduces activation barriers of surface reactions.

Selectivity of Si-OH Over Si-H Surface

$SiCl_3CH_3$

Transition State

Protected Si-OH Surface

HCl

Si-OH

E_A = 22.5 kcal/mol

ΔE = -6.4 kcal/mol

Transition State

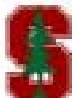
Unreacted Si-H Surface

HCl

Si-H

E_A = 65.3 kcal/mol

ΔE = 24.1 kcal/mol



Passivation reaction is unfavorable on Si-H terminated surface.

Effect of Cl Substitution and Selectivity

Selectivity of Surface Protection Reaction

Selectivity

1.0E+33
1.0E+30
1.0E+27
1.0E+24
1.0E+21
1.0E+18
1.0E+15
1.0E+12
1.0E+09
1.0E+06
1.0E+03
1.0E+00

200 300 400 500 600 700 800 900 1000 1100

Temperature (K)

SiCl(CH3)3
SiCl2(CH3)2
SiCl3CH3

Extremely high selectivity for Si-OH over Si-H terminated surfaces.

Growth of Nanowires on Si (100) with Styrene and Propylene

STM H abstraction to activate the surface

Activated Surface

$CH_2=CH-C_6H_5$

Styrene Adsorption

H abstraction to create a surface radical to propagate the chain reaction

Self-assembled molecular wires formed on Si (100)

Growth of Styrene Nanowires on Si (100)

0.0

-18.0
(-22.6)

21.0
(22.7)

3.5
(4.7)

-17.8
(-21.9)

-19.4
(-23.1)

Growth of Nanowires on Si (100) from Propylene

1. Applied STM Electric field

2. Activated Surface

$CH_2=CH-CH_3$

3. Propylene Adsorption

Self-Assembled molecular wires formed on Si (100) surface : Energy reduced by vdW (~3.3 kcal/mol per each pair)

Growth of Propylene Nanowires on Si (100)-2x1

0.0

-2.3
(-2.7)

15.5
(16.9)

4.6
(6.2)

-12.5
(-12.7)

-11.8
(-12.3)

Acknowledgements

Funding

- NSF
- SRC
- LSI Logic
- DARPA

Prof. Rick Garfunkel

Prof. Chris Chidsey