The Chemistry of ALD of High-K Dielectrics
Selection of Precursors, and Substrates

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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
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.
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
NH₃ on Si (100)-(2x1)

Insertion Mechanism:
1. NH₃(g) initially adsorbs on the “down” Si atom.
2. NH₃(a) dissociates into NH₂(a) and H(a).
3. NH₂(a) inserts into Si-Si dimer bond.
4. NH₂(a) dissociates into NH(a) and H(a).

- Insertion barrier is higher than desorption barrier.
- TPD (Chen, 1992)
  - 73% of NH₂(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:

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

Partition Functions:

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

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

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

The Hamiltonian:

The Schrödinger equation:

\[ \hat{H} |\psi\rangle = E |\psi\rangle \]

A lot of math and approximations:

Input:
Nuclear Coordinates, n and s.

The Variational Principle:

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

Basis functions:

\[ \phi_j = \sum_i c_i \phi_i \]

Basis functions:

1s 2s 3s 3p_x 3d^2 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:

<table>
<thead>
<tr>
<th>Method</th>
<th>RMS Error</th>
<th>MAD</th>
<th>RMS Error</th>
<th>MAD</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP (3)</td>
<td>3.59</td>
<td>10.8</td>
<td>2.25</td>
<td>7.01</td>
</tr>
<tr>
<td>G2 (7)</td>
<td>3.3</td>
<td>10.1</td>
<td>1.26</td>
<td>7.51</td>
</tr>
<tr>
<td>CCSD(T) (7)</td>
<td>2.61</td>
<td>4.4</td>
<td>1.4</td>
<td>3.6</td>
</tr>
<tr>
<td>KMLYP (3)</td>
<td>1.3</td>
<td>4.2</td>
<td>1.4</td>
<td>3.5</td>
</tr>
<tr>
<td>CBS-APNO (8)</td>
<td>1.26</td>
<td>4.4</td>
<td>1.2</td>
<td>3.3</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Candidate material</th>
<th>Formula</th>
<th>$\kappa$</th>
</tr>
</thead>
<tbody>
<tr>
<td>silicon oxide</td>
<td>SiO$_2$</td>
<td>3.5</td>
</tr>
<tr>
<td>silicon nitride</td>
<td>Si$_3$N$_4$</td>
<td>7</td>
</tr>
<tr>
<td>aluminum oxide</td>
<td>Al$_2$O$_3$</td>
<td>9</td>
</tr>
<tr>
<td>zirconium oxide</td>
<td>ZrO$_2$</td>
<td>25</td>
</tr>
<tr>
<td>hafnium oxide</td>
<td>HfO$_2$</td>
<td>30 - 40</td>
</tr>
</tbody>
</table>

**Candidate materials:**
ZrO$_2$, HfO$_2$, and Al$_2$O$_3$ 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

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TEM micrographs of Al$_2$O$_3$ 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

HfCl$_4$(g) + I$_2$O(g) → Hf-Cl* + Hf-OH* → HfO$_2$
**Comparison of ZrO$_2$ and HfO$_2$ ALD With MCl$_4$**

### MCl$_4$ Half-Reaction:

- **A:** $\text{ZrO}_2\text{-OH}^* + \text{ZrCl}_4 = \text{ZrO}_2\text{-O-Zr-Cl}^* + \text{HCl}$
- **B:** $\text{HfO}_2\text{-OH}^* + \text{HfCl}_4 = \text{HfO}_2\text{-O-Hf-Cl}^* + \text{HCl}$

### H$_2$O Half-Reaction:

- **A:** $\text{ZrO}_2\text{-O-Zr-Cl}^* + \text{H}_2\text{O} = \text{ZrO}_2\text{-O-Zr-OH}^* + \text{HCl}$
- **B:** $\text{HfO}_2\text{-O-Hf-Cl}^* + \text{H}_2\text{O} = \text{HfO}_2\text{-O-Hf-OH}^* + \text{HCl}$

**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).

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**HfO₂ ALD on SiO₂ and HfO₂ Substrates**

**HfCl₄ Half-Reaction:**
A: SiO₂-OH* + HfCl₄ = SiO₂-O-Hf-Cl* + HCl  
B: HfO₂-OH* + HfCl₄ = HfO₂-O-Hf-Cl* + HCl

**H₂O Half-Reaction:**
A: SiO₂-O-Hf-Cl* + H₂O = SiO₂-O-Hf-OH* + HCl  
B: HfO₂-O-Hf-Cl* + H₂O = HfO₂-O-Hf-OH* + HCl

- 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.

ZrCl$_4$ ALD Reactions on Multiple OH Sites on SiO$_2$

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

Pathway to trapped OH?
Hydroxylation of Ge(100) with H$_2$O

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

**Surface Preparation of Ge: Nitridation with NH₃**

Nitridation involves higher activation barriers.

_Nitridation must be done under non-equilibrium flow conditions because products are not most stable states in mechanism._

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

Energy (kcal/mol)

-40
-35
-30
-25
-20
-15
-10
-5
0
5
10

ZrCl$_4$ - Ads-OH-OH-Bridge
ZrCl$_3$-O-OH-Bridge
ZrCl$_2$-O-O-Bridge
HCl

Reaction on single Si-OH sites
Reaction on double Si-OH sites
OH-OH Dis
HfO$_2$ ALD Reactions Using Hf(NMe$_2$)$_4$

Will ALD growth rate be slower with Hf(NMe$_2$)$_4$ because it is larger than HfCl$_4$?
**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

<table>
<thead>
<tr>
<th>Bond Energies (kcal/mol)</th>
<th>O</th>
<th>Cl</th>
<th>N(CH$_3$)$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-X</td>
<td>114.22</td>
<td>95.04</td>
<td>91.52</td>
</tr>
<tr>
<td>Hf-X$_4$</td>
<td>121.09</td>
<td>103.51</td>
<td>81.03</td>
</tr>
</tbody>
</table>
HfO$_2$ ALD Reactions: Hf(NMe$_2$)$_4$ versus HfCl$_4$

Half-reaction with Hf(X)$_4$:

Hf(NMe$_2$)$_4$(g) + Hf-O-Hf-NMe$_2^*$

Half-reaction with H$_2$O:

Hf(NMe$_2$)$_4$(g) + H$_2$O(g) + Hf-Cl$_4$

Δ$E$ (kcal/mol)

-40 -30 -20 -10 0 10

Hf-O-Hf bridge is linear!

N dative bond to surface Hf

- Hf(N(CH$_3$)$_2$)$_4$ reaction is exothermic and does not exhibit trapping of intermediate state.
- Hf(N(CH$_3$)$_2$)$_4$ barrier is lower: lower ALD temperature.
- Hf(N(CH$_3$)$_2$)$_4$ 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)$_4$:

\[
\begin{align*}
\text{HfO}_2\text{-OH}^* + \text{Hf(N(CH}_3)_2\text{)}_4 & = \text{HfO}_2\text{-O-Hf-N(CH}_3\text{)}_2^* + \text{HN(CH}_3\text{)}_2 \\
\text{HfO}_2\text{-OH}^* + \text{Hf(N(CH}_3)_2\text{)}_4 & = \text{HfO}_2\text{-N(CH}_3\text{)}_2^* + \text{Hf(N(CH}_3\text{)}_2\text{)}_3\text{OH}
\end{align*}
\]

ALD Ligand-Exchange Reaction

Non-Growth Ligand Exchange

- Non-growth Ligand Exchange
  - results in lower growth rate
  - more competitive for MCl$_4$
  - may result in particle formation

\(\Delta E\) (kcal/mol)

Hf-N(CH$_3$)$_2^*$

Hf-O-Hf-NMe$_2^*$

Hf-OH$^*$

Hf-N(CH$_3$)$_2$OH(g)

Hf(NMe$_2$)$_4$(g)

Hf-O-Hf-NMe$_2$OH(g)

HNMe$_2$(g)
**Forward Reaction Rates**

- **HfCl$_4$ ALD Window**
  - 500°C
  - 350°C
  - 250°C
  - 150°C

**HfCl$_4$ reactions significantly Slower and require higher T.**

**Hf(N(CH$_3$)$_2$)$_4$ ALD Window**

**Rate of H$_2$O half-rxn too high - rate limiting step is DMA desorption leading to long purge times.**

<table>
<thead>
<tr>
<th>Reaction Type</th>
<th>Rate Constant ($k$)</th>
<th>Activation Energy ($E_a$)</th>
<th>Pre-Exponential Factor ($A$)</th>
<th>$E_a/R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HfCl$_4$ First Half-Reaction</td>
<td>2.81E+12</td>
<td>0.472</td>
<td>1.05E+04</td>
<td></td>
</tr>
<tr>
<td>HfCl$_4$ Second Half-Reaction</td>
<td>3.18E+11</td>
<td>0.450</td>
<td>9.05E+03</td>
<td></td>
</tr>
<tr>
<td>Hf(N(CH$_3$)$_2$)$_4$ First Half-Reaction</td>
<td>4.01E+12</td>
<td>0.017</td>
<td>5.68E+03</td>
<td></td>
</tr>
<tr>
<td>Hf(N(CH$_3$)$_2$)$_4$ Second Half-Reaction</td>
<td>5.72E+11</td>
<td>0.222</td>
<td>1.68E+03</td>
<td></td>
</tr>
</tbody>
</table>
HfCl$_4$ Forward and Reverse Reaction Competition

Etching reactions are significant

<table>
<thead>
<tr>
<th>Reaction Type</th>
<th>$A$</th>
<th>$n$</th>
<th>$E_a/R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HfCl$_4$ First Half-Reaction - Forward</td>
<td>2.81E+12</td>
<td>0.472</td>
<td>1.05E+04</td>
</tr>
<tr>
<td>HfCl$_4$ Second Half-Reaction - Forward</td>
<td>3.18E+11</td>
<td>0.450</td>
<td>9.05E+03</td>
</tr>
<tr>
<td>HfCl$_4$ First Half-Reaction - Reverse</td>
<td>1.51E+10</td>
<td>-0.321</td>
<td>2.34E+03</td>
</tr>
<tr>
<td>HfCl$_4$ Second Half-Reaction - Reverse</td>
<td>7.90E+11</td>
<td>0.197</td>
<td>2.69E+03</td>
</tr>
</tbody>
</table>
**Hf(N(CH₃)₂)₄ Forward and Reverse Reaction Competition**

Etching reactions are not significant

<table>
<thead>
<tr>
<th>Reaction Description</th>
<th>A</th>
<th>n</th>
<th>Eₜ/R</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hf(N(CH₃)₂)₄ First Half-Reaction - Forward</td>
<td>4.01E+12</td>
<td>0.017</td>
<td>5.68E+03</td>
</tr>
<tr>
<td>Hf(N(CH₃)₂)₄ Second Half-Reaction - Forward</td>
<td>5.72E+11</td>
<td>0.222</td>
<td>1.68E+03</td>
</tr>
<tr>
<td>Hf(N(CH₃)₂)₄ First Half-Reaction - Reverse</td>
<td>2.01E+09</td>
<td>0.344</td>
<td>9.72E+03</td>
</tr>
<tr>
<td>Hf(N(CH₃)₂)₄ Second Half-Reaction - Reverse</td>
<td>1.08E+12</td>
<td>0.341</td>
<td>1.28E+04</td>
</tr>
</tbody>
</table>
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.

HfCl$_4$

Hf[OCH$_2$CH$_3$]$_4$

*Linear O indicates double bonds to Hf*
ALD of HfO₂ with Hf(OEt)₄ and H₂O

Metal Half-Reaction

Hf(OEt)₄

Hf-OH*

TS-Hf-OH-EtOH

EtOH

Hf-O-Hf(OEt)₃*

Energy (kcal/mol)

-50

-40

-30

-20

-10

0

10

Ads-Hf-OH-Hf(OEt)₄

Trapped intermediates

Des-Hf-OEt-EtOH

Ethanol byproduct dative bonded to surface

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ALD of HfO₂ with Hf(OEt)₄ and H₂O

Oxygen Half-Reaction

H₂O

Hf-OEt*

TS-Hf-OEt-EtOH

Hf-Oh*

EtOH

RXN is endothermic

Des-Hf-OH-EtOH

Ethanol byproduct dative bonded to surface

Ads-Hf-OEt-H₂O
**ALD with HfCl$_4$ and Hf(OEt)$_4$ as Oxygen Source**

*High activation barrier!*

**Metal Half-Reaction**

- HfCl$_4$
- Hf-OEt$^*$
- TS-Hf-Cl-EtCl
- Hf-O-HfCl$_3^*$

Energy (kcal/mol):
- 30
- 20
- 10
- 0
- -10
- -20
- -30
- -40
- -50

**Ads-Hf-OEt-HfCl$_4$**
ALD with HfCl$_4$ and Hf(OEt)$_4$ as Oxygen Source

Oxygen Half-Reaction

High activation barrier!
Alternative Mechanism

Metal Half-Reaction

Two gas phase products:
- Favorable entropy at high T
- High barrier, endothermic
Alternative Mechanism for EtCl Elimination

Oxygen Half-Reaction

Two gas phase products
- Favorable entropy at high T
- High barrier and endothermic

Energy (kcal/mol)

Hf(OEt)₄ → TS-Hf-Cl-C₂H₄-HCl

Hf-Cl*  Hf-O-(OEt)₃*

C₂H₄  Des-Hf-OEt-HCl

Ads-Hf-Cl-Hf(OEt)₄

HCl
**Incomplete Cl Elimination**

**Oxygen Half-Reaction**

- **Hf(OEt)$_4$**
- **C$_2$H$_4$**
- **EtOH**
- **Hf-Cl$^*$**
- **Hf-O-(OEt)$_2$Cl$^*$**
- **Ads-Hf-Cl-Hf(OEt)$_4$**
- **Des-Hf-OEt-EtOH**
- **TS-Hf-Cl-C$_2$H$_4$-EtOH**

Energy (kcal/mol)

Incomplete Elimination!
Metal Oxide ALD Precursor Selection

**Metal chlorides:**
- Require high temperatures
- Almost thermal neutral
- Lead to trapped intermediates
- Readsoption 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
**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

Alkylamide ALD on Amine Terminated SAM?

- NH₂ SAM

Al[N(CH₃)₂]₃

Al[N(CH₃)₂]₃-NH₂ SAM complex

TS

TMA

- Alkylamide precursor should allow even lower growth T.

- Other metal reactions for forming contacts to molecular electronic devices?

- ALD on NH terminated surfaces?
$HfO_2$ ALD on NH* Terminated Si and Ge

Al[N(CH$_3$)$_2$]$_3$

Si-NH* surface

NH(CH$_3$)$_2$

TMA-complex

CH$_4$

Energy (eV)
Hf Nitride or Oxynitride ALD?

- Energy (eV)
  - NH$_3$
  - HfN(CH$_3$)$_2$ * site
  - TS
  - NH(CH$_3$)$_2$
  - Hf[N(CH$_3$)$_2$]$_4$
  - Hf-NH$_2$ * site
  - TS
  - NH(CH$_3$)$_2$
  - Hafnium amide-complex
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)
Acknowledgments:

Students: Yuniarto Widjaja, Collin Mui, Joseph Han, Ye Xu

Collaborators: Roy Gordon (Harvard), Steve George (Colorado), Rick Garfunkel (Rutgers), Stacey Bent (Stanford)

INTEL, Novellus, Motorola, Texas Instruments, Torrex, Applied Materials

CEBSP (NSF, SRC), MARCO (SRC, DARPA), ONR