Simulation of High-K Gate Deposition

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Yamaguchi, APL, 2002
MOSFET Scaling

- Metal-Oxide-Semiconductor (MOS) structure

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

Green at al., J. Appl. Phys, 2001, adapted from ITRS
**Gate Leakage Due to Electron Tunneling**

**Current Technology:**
- Leakage current from electron tunneling increasing exponentially as gate dielectric thickness decreases.

\[ C = \frac{\kappa \varepsilon_0}{t} \]

**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.
**High-K Choices**

<table>
<thead>
<tr>
<th>Dielectric Materials</th>
<th>Dielectric Constant, $\kappa$</th>
</tr>
</thead>
<tbody>
<tr>
<td>silicon oxide</td>
<td>SiO$_2$, 3.5</td>
</tr>
<tr>
<td>silicon nitride</td>
<td>Si$_3$N$_4$, 7</td>
</tr>
<tr>
<td>aluminum oxide</td>
<td>Al$_2$O$_3$, 9</td>
</tr>
<tr>
<td>zirconium oxide</td>
<td>ZrO$_2$, 25</td>
</tr>
<tr>
<td>hafnium oxide</td>
<td>HfO$_2$, 30 - 40</td>
</tr>
</tbody>
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- ZrO$_2$, HfO$_2$, and Al$_2$O$_3$ are favorable candidates for the gate dielectric
  - High-$\kappa$
  - 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$_2$
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.

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.

\[ \psi(1, 2, \ldots, n) = \begin{vmatrix} \phi_1(x_1) & \phi_2(x_1) & \cdots & \phi_n(x_1) \\ \phi_1(x_2) & \phi_2(x_2) & \cdots & \phi_n(x_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(x_n) & \phi_2(x_n) & \cdots & \phi_n(x_n) \end{vmatrix} \]

The Schrödinger equation

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

The Variational Principle

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

\[ \phi_j = \sum_{i} c_i \phi_i \]
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

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

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

\[ \text{NH}_3(g) + \text{SiH}_4(g) \rightarrow \text{Si-NH}_2(a) + \text{H}_2(g) \]

\[ \text{E}_a = 59 \text{ kcal/mol} \]

Reactions on N-H sites

\[ \text{SiH}_4(g) + \text{H}_2(g) \rightarrow \text{SiH}_2(a) + \text{H}_2(g) \]

\[ \text{E}_a = 49 \text{ kcal/mol} \]
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
Initial Oxidation Reaction Mechanism

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

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\[ \Delta E \text{ (kcal/mol)} \]

- \( \Delta E = 35 \) kcal/mol for \( \text{O}_2(a) \) adsorbed state
- \( \Delta E = 33 \) kcal/mol for \( \text{O}_2(b) \) peroxide bridge
- \( \Delta E = 36 \) kcal/mol for \( \text{O}(sb)-\text{O}(a) \)
- \( \Delta E = 67 \) kcal/mol for \( \text{O}(sb)-\text{O}(bb) \)

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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 SiO₂ below ZrO₂

The ALD Process

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

TEM micrographs of Al₂O₃ obtained with ALD and conventional MOCVD process (courtesy of IPS-Tech)
Zirconium Oxide ALD

\[ \text{ZrCl}_4(g) + \text{H}_2\text{O}(g) \rightarrow \text{Zr}-\text{Cl}^* + \text{Zr}-\text{OH}^* \]

\[ \text{Zr}-\text{Cl}^* + \text{Zr}-\text{OH}^* \rightarrow \text{ZrO}_2 \]
**ZrO$_2$ ALD Reaction with Zr-OH* Sites**

**Reactants**
- Zr-OH* + ZrCl$_4$(g)

**Products**
- Zr-O-ZrCl$_3$* + HCl(g)

**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$_2$O and one Cl atom from ZrCl$_3$
4. HCl desorbs

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**ZrO₂ ALD Reaction with Zr-Cl* Sites**

**Trapping-mediated pathway:**

1. Zr-Cl*-H₂O complex is formed
2. HCl(a) formation transition state
3. HCl(a) is formed from one H atom from H₂O and one Cl atom from ZrCl₃
4. HCl desorbs
Comparison of the 1st & 2nd Half-reactions of ZrO₂ ALD

Zr-OH* + ZrCl₄(g) + HCl(g) → Zr-O-ZrCl₃* + HCl(g)

Zr-O-ZrCl₃*-HCl complex

HCl TS

Zr-Cl* + H₂O(g) → Zr-Cl*-H₂O complex

Zr-OH*-HCl complex

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Comparison of the 1st & 2nd Half-reactions of HfO₂ ALD

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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 \( \text{ZrCl}_4(\text{g}) \) 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)

\[
\text{Si-H}* + \text{ZrCl}_4(\text{g}) \rightarrow \text{Zr-Cl}* + \text{HCl}(\text{g})
\]

\[ E_a = 53 \text{ kcal/mol} \]
\[ \Delta H = 31 \text{ kcal/mol} \]

Copel et al., APL, 2000
Reactor of ZrCl4 on OH Terminated SiO2

- ZrCl4 reacts with Si-OH* surface sites to form a Si-OH-ZrCl4 intermediate, followed by HCl evolution and formation of a Si-O-Zr-Cl* surface site.

![Reaction Diagram](image-url)
**Reaction of H\(_2\)O with the Zr-Cl\(^*\) Surface Site**

1. Zr-Cl\(^*\)-H\(_2\)O complex is formed
2. HCl(a) is formed from one H atom from H\(_2\)O and one Cl atom from ZrCl\(_3\)
3. HCl desorbs

The H\(_2\)O complex is very stable!
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$_2$O:
A: Si-O-Zr-Cl$^*$ + H$_2$O = Si-O-Zr-OH$^*$ + HCl
B: Zr-O-Zr-Cl$^*$ + H$_2$O = Zr-O-Zr-OH$^*$ + HCl

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

Issues: Trapping at the intermediate state.
Zr\textsubscript{4}Cl\textsubscript{4} on the Si(100)-(2x1) Surface

- ZrCl\textsubscript{4} dissociates into ZrCl\textsubscript{3}(a) and Cl(a) on the Si(100)-(2x1) surface
- This results in Zr-Cl\textsuperscript{*} and Si-Cl\textsuperscript{*} surface sites

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

Structure of ZrCl\textsubscript{4}(a) has not been obtained. However, $\Delta H_{\text{ads}}$ is estimated to be similar to $E_{\text{TS}}$.
**Reaction of H\textsubscript{2}O with the Zr-Cl\textsuperscript{*} Surface Site**

Reaction of H\textsubscript{2}O with the Zr-Cl\textsuperscript{*} site results in a Zr-OH\textsuperscript{*} site in place of the Zr-Cl\textsuperscript{*} site.

**Trapping-mediated mechanism:**

1. Zr-Cl\textsuperscript{*}-H\textsubscript{2}O complex is formed
2. HCl(a) is formed from one H atom from H\textsubscript{2}O and one Cl atom from ZrCl\textsubscript{3}
3. HCl desorbs

The H\textsubscript{2}O 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$_2$O 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*
**Mechanism of First Half Reaction**

- TMA adsorbs molecularly on to Al-OH* surface site
- -CH₃ group from TMA reacts with H atom from surface –OH*
- Desorption of CH₄ and formation of -O-Al-(CH₃)₂*

\[ \text{Al-OH}^* + \text{Al(CH₃)₃} \rightarrow \text{Al-O-Al-CH₃}^* + \text{CH₄} \]
Quantum Chemical Study of $\text{Al}_2\text{O}_3$ ALD

Mechanism of Second Half Reaction

- $\text{H}_2\text{O}$ adsorbs molecularly on to $\text{Al}-(\text{CH}_3)_2^*$ surface site
- $\text{-CH}_3$ group from surface site reacts with $\text{H}$ atom from $\text{H}_2\text{O}$
- Desorption of $\text{CH}_4$ and formation of $\text{Al-OH}^*$

$\text{Al}-\text{CH}_3^* + \text{H}_2\text{O} \rightarrow \text{Al-OH}^* + \text{CH}_4$

$\text{Al}_2\text{O}_3$ ALD reaction mechanisms (Second Half Reaction)
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 $H_2O/H_2O_2$

$E$ (kcal/mol)

PES of step 1a (Ge$_9$ and Ge$_2$Si$_7$ clusters)

$H_2O/H_2O_2 + Ge(100)$

$H_{(ads)} + OH_{(ads)}$

$2OH_{(ads)}$

$Ge9+H2O$  $Ge9+H2O2$  $Ge2Si7+H2O$  $Ge2Si7+H2O2$
ZrCl₄ Initial Reaction on Ge-OH

\[ 2 \text{OH}_{(ads)} + \text{ZrCl}_4 \rightarrow \text{TS7} \rightarrow \text{TS8} \rightarrow \text{PES of step 1b (Ge}_9 \text{ cluster)} \]

\[ \text{TS7} \rightarrow \text{TS8} \rightarrow \text{Ge}[\text{OZrCl}_2\text{O}] + 2\text{HCl} \]

\[ \text{a-Ge}[\text{OZrCl}_2\text{O}]\text{-HCl} + \text{HCl} \rightarrow \text{Ge}[\text{OZrCl}_3\text{OH}] + \text{HCl} \]

\[ \text{a-Ge}[\text{OZrCl}_3\text{OH}] - \text{HCl} \rightarrow \text{PES of step 1b (Ge}_9 \text{ cluster)} \]
Bridging Across the Trench

6.3 kcal mol\(^{-1}\) more stable

19.2 kcal mol\(^{-1}\) more stable
Summary

• Detailed mechanisms proposed for ZrO₂, HfO₂ and Al₂O₃ ALD reactions. Additional reactions (for example elimination of H₂O 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.

• Al₂O₃ ALD using TMA should have higher growth rates (monolayers/cycle).

• Calculations indicate that the hydroxylation of Ge surfaces with H₂O₂ is kinetically more favorable.

• ALD with ZrCl₄ 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.
Yuniarto Widjaja
CHARLES POWELL FOUNDATION, MOTOROLA, STANFORD, DARPA, SRC MARCO MSD Center

Acknowledgments:
A graduate student Potential Energy Surface

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