Surface Modification for Selective Atomic Layer Deposition of High-κ Dielectric Materials

Collin Mui and Stacey F. Bent
Department of Chemical Engineering

Charles B. Musgrave
Departments of Chemical Engineering and Materials Science and Engineering

Stanford University, Stanford CA 94305-5025

NSF/SRC Engineering Research Center for Environmentally Benign Semiconductor Manufacturing
1. Moore’s Law and Transistor Scaling

**Moore’s Law:** The number of transistors in integrated circuits doubles every 18 months.

**Transistor Scaling:** Decrease dimensions to maintain constant electric field in the device, including the gate oxide thickness.

- Frequency Response $\propto \frac{1}{L}$
- Dimensions $(L, t) \propto \frac{1}{K}$
- Gate Capacitance $\propto \frac{1}{K}$
2. The Need for High-\(\kappa\) Dielectric Materials

Leakage current through electron tunneling increases exponentially when the dielectric film thickness is decreased.

Replacing SiO\(_2\) with high-\(\kappa\) dielectric materials allows thicker gate dielectrics and hence reduces leakage currents.

<table>
<thead>
<tr>
<th>Dielectric Materials</th>
<th>(\kappa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>silicon oxide</td>
<td>SiO(_2)</td>
</tr>
<tr>
<td>silicon nitride</td>
<td>Si(_3)N(_4)</td>
</tr>
<tr>
<td>aluminum oxide</td>
<td>Al(_2)O(_3)</td>
</tr>
<tr>
<td>hafnium oxide</td>
<td>HfO(_2)</td>
</tr>
<tr>
<td>zirconium oxide</td>
<td>ZrO(_2)</td>
</tr>
</tbody>
</table>

Capacitance \(\propto \frac{\kappa}{t}\)

• How to deposit high-\(\kappa\) materials?
• How to deposit high-\(\kappa\) materials in an environmentally benign manner?
3. Atomic Layer Deposition (ALD)

- ALD occurs through a binary sequence of **self-limiting** surface reaction steps.
- Each step deposits an **atomic layer** of thin film material.

**Advantages of ALD**
- Accurate and simple thickness control
- Excellent conformality and reproducibility
- High quality materials
- Possibility for interface modification

**Applications of ALD**
- High-\(\kappa\) dielectrics for gate stacks
- Metallic lines for interconnects
- Diffusion barriers
4. Examples of ALD Surface Chemistry

**ZrO₂ Deposition**

- **H₂O**
- **ZrCl₄**
- **OH OH OH OH OH OH OH**
- **ZrCl₃ ZrCl₂ ZrCl₃ ZrCl₂ ZrCl₃**
- **Zr**

**W Deposition**

- **WF₆**
- **WF₆**
- **WF₆**
- **Si₂H₆**
- **WFₓ WFₓ WFₓ WFₓ**
- **SiₓFᵧ SiₓFᵧ SiₓFᵧ SiₓFᵧ**
- **W**

**SiHₓFᵧ**
5. Environmentally Benign Selective ALD

Subtractive Processing vs. Additive Processing

Deposit high k dielectric and metal gate

Spin-on imaging layer

Photolithography

Develop in aqueous base

Etch metal

Strip Imaging layer

Deposit and pattern field oxide

Deactivate field oxide surface

Photolithography eliminated

Wet chemistry eliminated

Activate Si surface

Selectively deposit high k dielectric

Courtesy: Dr. Muscat
6. Process Flow for Selective ALD (con’t)

Subtractive Processing vs. Additive Processing

- Spin-on imaging layer
- Photolithography
- Develop in aqueous base
- Etch dielectric
- Strip Imaging layer
- Deposit and pattern field oxide

Selectively deposit metal gate

Activate high k surface

Photolithography eliminated
Wet chemistry eliminated
Plasma etching eliminated
Wet chemistry eliminated

Reduce processing steps & Minimize ESH impact

Courtesy: Dr. Muscat
7. Selective ALD of High-κ Dielectric

HF followed by H₂O

(a) 

(b) 

(c) 

(d) 

(e) 

Cleaned and patterned Si → Protect oxide → Si surface activation → Maskless, selective ALD
8. Combination of Experiment and Theory

Multiple Internal Reflection
Fourier Transform
Infrared Spectroscopy

UHV System

C-H Stretch

Si Crystal

Quantum Chemistry Calculations

Schrödinger equation
\[ \hat{H} \Psi = E \Psi \]

Density functional theory

Energy $E$

Geometry $\frac{\partial E}{\partial R_\alpha}$

Frequency $\frac{\partial^2 E}{\partial R^2_\alpha}$

NSF/SRC Engineering Research Center for Environmentally Benign Semiconductor Manufacturing
9. Surface Modification for Selective ALD

Modified Si Surface

Protected Oxide

ALD High-κ Dielectric

SiO₂

OH OH OH OH
H H H H

Si-H

R-X

Cl₂

Activated Si-Cl

Protected SiO₂

R R R
O O O O
H H H H

Unreacted Si-H

Protected SiO₂

R R R
O O O O
Cl Cl Cl Cl

NSF/SRC Engineering Research Center for Environmentally Benign Semiconductor Manufacturing
10. Strategies for Protecting SiO₂

**Hexaalkyldisilazane**

```
R-Si-N-Si-R
R-H-R
```

**Alkylchlorosilanes**

```
R-Si-R
Cl
```

```
R-Si-R
O
```

```
R-Si-R
Cl
```

```
R-Si-R
O
```

**Formation of self-assembled monolayers on SiO₂ in vacuum?**

**NSF/SRC Engineering Research Center for Environmentally Benign Semiconductor Manufacturing**
11. Reactivity of N Lone Pair on Si(100)

Trimethylamine Physisorption and Chemisorption

Trimethylamine Reactant

Trans lone pair effect (Bohlman bands)

Molecular Chemisorption

Si-N dative bond

Wavenumber (cm⁻¹)

Absorbance

(CH₃)₃N on Si(100)-2x1

(a)

3400 3200 3000 2800 2600 2400

(b)

0.0005

110 K

300 K
12. Chemistry of Amines on Si(100)

Trimethylamine
No N-H bonds, N-CH₃ cleavage unfavorable.  
Molecular chemisorption through lone pair.

Dimethylamine
Similar to HMDS, has N-H functionality.  
N-H dissociation on Si(100).
Methyamine behaves the same.
13. Reaction of Hexamethyldisilazane

**Reaction of H₂O at 300 K generates Si-H and Si-OH surface groups.**

- Expose 0.1 mtorr HMDS to Si-OH covered surface at 300 or 440 K for 30 min.
- Record IR spectra at 300 K.

**Experimental observations**

- Reacts on clean Si(100).
- Reacts with Si-OH even at 300 K.
- Some selectivity for Si-OH over Si-H.
14. Modeling SiO₂ Surface and Si-OH Groups

Example: Surface chemistry for silicon oxide ALD

Attachment chemistry is localized at the surface functional group.

NSF/SRC Engineering Research Center for Environmentally Benign Semiconductor Manufacturing
15. Reaction of Alkylchlorosilanes (Theory)

Cl substitution reduces activation barriers of surface reactions.

NSF/SRC Engineering Research Center for Environmentally Benign Semiconductor Manufacturing
16. Reaction of Alkylchlorosilanes (Experiments)

**Alkylchlorosilanes**
- Contain Si-Cl functional group.
- Commonly used to form siloxane bonds.
- Forms SAMs on SiO₂ surfaces.

**Experimental Results**
- TCES spectrum shows loss of Si-OH stretch and growth of C-H stretch.
- CTMS spectrum shows no reaction.

**Future Work**
- Verify selectivity on Si-H covered surface.
- Try other functional groups (SiCl₂R₂).
- Reactivity toward subsequent steps.
17. Selectivity of Si-OH Over Si-H Surface

Passivation reaction is unfavorable on Si-H terminated surface.

NSF/SRC Engineering Research Center for Environmentally Benign Semiconductor Manufacturing
18. Effect of Cl Substitution and Selectivity

Extremely high selectivity for Si-OH over Si-H terminated surfaces.
19. Where Can This Go in the Future?

- HF followed by H₂O
- RSiCl₃
- Cl₂
- SiF₄
- WF₆

- Protect oxide
- Si surface activation
- Selective ALD of ZrO₂
- ALD of W metal gate
Conclusions

- Selective ALD is an environmentally benign method to deposit high-κ dielectric materials.
- Hexamethyldisilazane, which contains N-H bonds, reacts on both clean and Si-OH covered Si(100).
- We have shown successful attachment of alkylchlorosilane to surface Si-OH groups.
- DFT calculations show high selectivity of alkylchlorosilane on surface Si-OH over Si-H groups.
- Selective ALD of metal gate on high-κ dielectric in the future!