The relation between crystalline phase, electronic structure and dielectric properties in high-K gate stacks


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Scaling the MOSFET Gate Stack Structure

SiO₂ Dielectric?

Si₃N₄ Spacers

High-k Dielectric

Future Gate Structure

- Si-compatible high-k dielectric
- Barrier layers and stacked structures
- New electrode: Ge doped Si, metal, metallic oxide or nitride
- EOT 10⇒5Å?
Benefit of integrating high-k material in CMOS devices

- **Reduction in tunneling current**
- **Less power dissipation**

**Oxide Thickness**
- 5.6 nm
- 3.5 nm
- 3.0 nm
- 2.5 nm

**Equation**

\[ J \alpha T^2 \exp \left( \frac{q}{kT} \left( -\phi_B + \sqrt{\frac{qE}{4\pi\epsilon_i}} \right) \right) \]

\[ J \alpha E \exp \left( \frac{q}{kT} \left( -\phi_B + \sqrt{\frac{qE}{\pi\epsilon_i}} \right) \right) \]

\[ J \alpha \frac{q^3 E^2}{\phi_B} \exp \left( -c \left( \frac{q\phi_B}{qE} \right)^{\frac{3}{2}} \right) \]

**Trade-off:** \( \phi_B \) thickness

G. D. Wilk, et.al, JAP 89, 5243 (2001)
Benefits of using a high-k material

High-κ film ⇒ thicker gate dielectric ⇒ lower leakage w/ same performance

\[ C_{ox} = \frac{\kappa \varepsilon_0 A}{t_{ox}} \Rightarrow t_{\text{high-κ}} = \left( \frac{\kappa_{\text{high-κ}}}{\kappa_{\text{SiO}_2}} \right) \cdot t_{\text{SiO}_2} \]
How to locate the valence and conduction band positions?

- Theoretical density of states (probably the best method)

\[ N_{v}(E) = \int_{0}^{\infty} n_{v}(E') g(E - E') dE' \]

Response function

Theoretical DOS
Phase Diagram for HfO$_2$

5 identified phases of HfO$_2$

- Cubic
- Tetragonal
- Orthorhombic I
- Orthorhombic II
- Meta-stable

May be stabilized by:
- film stress
- grain-size effects
- impurities

Monoclinic - stable phase at ambient temperature and pressure
Density of States for all phases of HfO$_2$

- Band gap values are different for phases!
- Effects on band alignment?

Crystal structure can have considerable effect on measured band gap and hence barrier heights.
**Approach:**

XRD, XAS, HRTEM, FTIR – for phase identification

DFT calculations – to determine DOS for the identified phase

Photoemission (PES) using soft x-rays – for mapping occupied densities of states

Inverse Photoemission (IPES) – for unoccupied densities of states

**Sample preparation:**

CVD HfO$_2$ using Hf-tetra-tert.-butoxide 400C in the thickness regime of 10 Å - 1µ

ALD ZrO$_2$ using ZrCl$_4$/H$_2$O chemistry at 300C in the thickness regime of 30-100 Å

**Photoemission Spectroscopy (PES):**
Brookhaven National Laboratories – beamline U8b (100-350 eV)

**Inverse Photoemission Spectroscopy** IPES:
Rutgers University (15-40 eV)
Inverse Photoemission Spectroscopy (IPES)

- IPES provides information on states above Fermi level
- Mapping of unoccupied states is possible
- Complementary technique to photoemission (PES)
XRD Studies on HfO$_2$/SiO$_{x}$N$_{y}$/Si gate stack

Crystal structure – film thickness

- Thicknesses are determined by Rutherford Backscattering Spectroscopy (RBS)

- The diffraction peak positions are consistent with monoclinic structure

- As the films get thinner, average crystal size decreases, indicating more disorder
Partial DOS for monoclinic HfO$_2$

- 3-fold coordinated O (1)
- 4-fold coordinated O (2)

- Valence band is predominantly composed of O-like bands
- Valence band edge is determined by three-fold coordinated O
- Conduction band is predominantly – Hf d-like bands
Results of combined photoemission and inverse photoemission studies

- Valence band is predominantly composed of O-like bands
- Conduction band is predominantly – Hf d-like bands
Locating Valence Band Maximum (VBM) and Conduction Band Minimum (CBM)

- Extract VBM and CBM from band structure calculations

- Agreement between theory and experiment is remarkable (width of bands, and main features)

- Even though the DOS is not corrected for PES and IPES cross-sections

- However note the disagreement between theory and experiment close the band edges
Results from combined theory and experiment

- Theoretical DOS is convoluted with the appropriate response function

- VBM and CBM energy positions are extracted from band structure calculations

- Electron affinity for HfO₂ is ~2.2 eV

- Using the position of Fermi level within silicon gap

- Φₙ~2.0 eV and Φₜ~3.6 eV – sufficiently large from leakage point of view
Band-tail-States – “Effective” band gap

Order to disorder transition

Can result from:
- Crystal imperfections
- Defects
- Impurities
- Stoichiometry

• Theory and experiment comparison yielded a gaussian distribution of these states centered close to band edges
Defect – edge transitions - the effective gap and barriers

• Therefore intrinsically the perfect crystals have larger band gap

• However due to the presence of band-tail-states, gap is reduced

• Concept of “effective” gap as well as barrier heights can be more meaningful

• XRD reveals that the films are predominantly monoclinic

• Therefore finite crystallinity

• On the other hand, theoretical calculations considers perfect crystal

• Disorder in the film will result in appearance of band-tail states
• A perfect HfO$_2$ crystal intrinsically has a larger band gap (than reported to date)

• The presence of defect states close to band edges results in a smaller “effective” band gap and barrier heights
Summary of band alignment for HfO$_2$/SiO$_2$/p-Si gate stack

- Occupied and unoccupied densities of states of HfO$_2$ is studied by PES and IPES
- VBM and CBM are located by combining theoretical calculations with expt data
- Comparison of theory and experiments suggested presence of band tail states in proximity of band edges
- Due to the presence of band tail states, concept of “effective” band gap may be more meaningful
- The extracted “effective” band gap, electron affinity and barrier heights are 5.84, 2.68, 1.47 and 3.25 eV
Develop understanding of the electronic structure of different crystal phases of HfO$_2$ and ZrO$_2$ and the effect of annealing on physical and electronic properties

**Background:** Compare HfO$_2$ and ZrO$_2$, and show results of relevance to phase and electronic structure issues in gate stack engineering

**One Problem:** A broad range of dielectric constants, band gaps and barrier heights are reported in the literature.

**Question:** Can the phase of ZrO$_2$ (present in different films prepared by different deposition techniques and anneals) be responsible for the difference in measured values?

**Solution:** Use array of experimental methods and DFT calculations to determine phase and electronic properties.

**DFT calculations:** excellent for structure and energetics but underestimates the true band gaps however, consistent and comparable.
Dielectric Constant for Different Phases of ZrO$_2$

<table>
<thead>
<tr>
<th>Phase</th>
<th>Static Dielectric Tensor</th>
<th>(\varepsilon_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic Phase</td>
<td>(\varepsilon_{\text{cubic}} = \begin{pmatrix} 31.8 &amp; 0 &amp; 0 \ 0 &amp; 31.8 &amp; 0 \ 0 &amp; 0 &amp; 31.8 \end{pmatrix})</td>
<td>(\sim 37)</td>
</tr>
<tr>
<td>Tetragonal Phase</td>
<td>(\varepsilon_{\text{tetra}} = \begin{pmatrix} 41.6 &amp; 0 &amp; 0 \ 0 &amp; 41.6 &amp; 0 \ 0 &amp; 0 &amp; 14.9 \end{pmatrix})</td>
<td>(\sim 47)</td>
</tr>
<tr>
<td>Monoclinic Phase</td>
<td>(\varepsilon_{\text{mono}} = \begin{pmatrix} 16.7 &amp; 0 &amp; 0.98 \ 0 &amp; 15.6 &amp; 0 \ 0.98 &amp; 0 &amp; 11.7 \end{pmatrix})</td>
<td>(\sim 20)</td>
</tr>
</tbody>
</table>

Static dielectric tensor =
purely electronic screening (10-25%) +
lattice contribution (IR-active phonons, 75-90%)
Dielectric constant and Band Gap of all phases of HfO$_2$ and ZrO$_2$

- Tetragonal phase of both oxides have high dielectric constant and band gap
- If tetragonal thin ZrO$_2$ can be prepared, full advantage can be taken
- HfO$_2$ has a higher band gap than ZrO$_2$ (~0.6 eV) for the same phase
Summary of theoretical calculations

- Crystal structure can have considerable effect on measured permittivity, band gap and barrier heights
- Crystal structure of thin films needs to be determined and stated in studies
- Tetragonal phase of both oxides have high dielectric constant and band gap

Thermal anneal effects

- Permittivity
- Band gap
- Barrier heights

Stabilization of a certain phase due to:
- Film stress
- Grain-size effects
- Impurities
• Can tetragonal ZrO$_2$ be prepared (in gate stack)?

![Graph showing dielectric constant and band gap for HfO$_2$ and ZrO$_2$.]

• Tetragonal phase of both oxides have high dielectric constant and band gap.
Density of States for all phases of ZrO$_2$

- Band gap values are different for phases!

- Crystal structure can have considerable effect on measured band gap and hence barrier heights

- Effects on band alignment???
If tetragonal phase can be prepared, a high dielectric constant and band gap should be expected.

A couple of approaches:

1. Increasing the coordination of metal cation (Hf, Zr)
2. Move to conditions where tetragonal thermo. dominate
3. Lock in metastable phase kinetically.

In monoclinic structure, Zr is 7-fold coordinated.

High temperatures are required for the desired phase stabilization.
- Melting and transformation temperature depends on the radius of crystallites

- Small crystallite size, decreases the transformation temperature

Nanocrystallite size effect on the P–T Phase Diagram

Gibbs – Thomson Relationship

\[
\frac{T - T_0}{T_0} = - \frac{2V_T}{\Delta H_{M-T}} \frac{1}{\sigma} \frac{1}{r}
\]

- Melting and transformation temperature depends on the radius of crystallites
- T, P, and grain size plays an important role in the stabilization of the tetragonal form

Pitcher, Ushakov, Novratsy, to be published.
XRD Studies on ALD ZrO$_2$ thin films

- Crystal structure – film thickness dependence is studied by wide angle x-ray scattering WAXS.

- The 62 Å films is found to be predominantly amorphous.

- XRD spectra of thicker films are consistent with tetragonal phase of ZrO$_2$. 
How to Identify the Phase of Thin Films by X-ray Absorption Spectroscopy (XAS)

- \( L_{2,3} \) edges of transition metals (T) serve as a direct probe of empty T-d states, as well as the crystal structure.

\[
\mu(E) = \sum_{\text{final states}} \left| \langle \Psi_f | \hat{H} | \Psi_i \rangle \right|^2 \rho(E_f)
\]

- \( \mu(E) \) = dipole/quadrupole operator

- \( i \) = core level
- \( f \) = empty d-states

- **Approach**: Comparison with reference materials of known crystal structure
Phase Identification of ZrO\textsubscript{2} films by XAS

- XAS L\textsubscript{2} and L\textsubscript{3} edges of Zr are dominated by transitions into unoccupied Zr-4d states.

- XAS of ZrO\textsubscript{2}/SiO\textsubscript{2}/Si compared with reference materials of known crystal structure

- Zr- L\textsubscript{2}, L\textsubscript{3} edge measurements provide a convenient tool for identifying the structural changes in ZrO\textsubscript{2} films.
XAS L₂ and L₃ edges of Zr are dominated by transitions into unoccupied Zr-4d states.

Thin film (53 Å) spectrum is not consistent with any of the known phases of ZrO₂.

XRD on thin films indicate amorphous structure.

The spectrum for the thicker film (81 Å) is consistent with that of the tetragonal phase.

Spectrum obtained for the 53 Å films following 600°C thermal anneal is consistent with that of tetragonal phase.

Zr-L₂ edge measurements provide a convenient tool for identifying the structural changes in ZrO₂ films.
Thermal Anneal Effects on Crystal Structure of ZrO₂ Film Studied by XAS

- Thermal anneals resulted in phase change as apparent from the XAS measurements

Amorphous → Tetragonal
Two important trends:
- Thickness
- Thermal anneals

As thickness of the as-deposited films increase above some transitional value, bandgap increases from 5.1 eV to 5.5 eV.

The bandgap of the thin sample increased after being annealed to 600°C.
In this thickness regime, there is a transition from an amorphous to a tetragonal phase. There is some transitional value (65-75Å optical thickness) at which this occurs.
XAS, SE and FTIR studies on ALD ZrO$_2$

**Zr L$_2$-edge**

As thickness increases:
- Crystal structure becomes tetragonal
- Bandgap increases
- Dielectric function increases

**Ellipsometry (SE)**

**FTIR**

XAS, SE and FTIR for high-$\kappa$ materials:
- Powerful
- Non-destructive
- Complimentary techniques
Summary

• **It is desirable to make tetragonal ZrO$_2$ ($\varepsilon_0 \sim 35$).**
  (i) Tailoring films thickness
  (ii) Annealing
  (iii) Impurities (e.g. cubic ZrO$_2$)

• **Important consequences:**
  (i) Higher $\varepsilon_0$, lower EOT
  (ii) Larger bandgap, different band offsets, affects charge transport
  (iii) Metrology: determination of true dielectric constant, thickness

• **Issues:**
  (i) Crystal sizes, leakage
  (ii) Gate length vs crystal sizes
  (iii) Phase variations in the dielectric and channel mobility
  (iv) In addition to coulomb and phonon scattering, potential variations in the channel due to existence of multiple phases)
The crystal structure for ZrO₂ is determined to be amorphous

\[ \Delta E_g \approx 0.6 \text{ eV} \]

Difference originating from final state effects

Band gap measurements of ZrO₂ – PES/IPES vs. Ellipsometry

Photon Energy (eV)

\[ E_g = 5.05 \text{ eV} \]
FINAL REMARKS:

**Issues regarding band gap and band offset determination:**
Measurement of $E_g$ and $\phi_e$, $\phi_h$ will depend on:
- Crystal structure
- Method used (PES/IPES, SE, etc..) – Question: which is more relevant???
- Band tail states – how to include in the effective values

**Issue regarding dielectric constant determination**
- Film thickness regime – key factor in regulating crystal structure
- Crystal structure
- Processing history
- Impurities, stress – effect on stabilizing crystal structure

**Non-destructive analytical techniques for crystal structure determination:**
- Zr-L$_2$ edge XAS measurements provide a convenient and sensitive tool for identifying the structural changes in these ZrO$_2$ films.
- FTIR – Grazing angle total attenuated reflectance: powerful technique to study phonon modes
Soft x-ray photoemission spectrum of 28Å HfO₂/SiO₂/p-Si gate stack

- Hf 4f spin-orbit doublet – Hf 4f<sub>7/2</sub> binding energy 17.65 eV
- Hf 4f<sub>7/2</sub> – VBM energy separation = 14.14 eV
Si 2p binding energy shifts
~0.26 eV towards higher BE

• Consistent with downward band bending in Si

• Downwards band bending for p-Si indicates presence of negative charge
Estimation of charge from band bending

- Using the measured band bending and $N_A = 1 \times 10^{15} \text{ cm}^{-3}$
- The charge can be calculated $Q_s \approx 9.5 \times 10^{-7} \text{ C/cm}^2$

This is in good agreement with the reported value*

$Q \approx -6 \times 10^{12} \text{ cm}^{-2}$

* E. Cartier et.al. “Characterization of the $V_t$-instability in SiO$_2$ / HfO$_2$ gate dielectrics”
Origin of observed band bending - Electrostatics

Electrochemical potential equalization results in charge transfer to silicon, therefore band bending occurs to accommodate this charge.

If the local workfunction at the surface could be probed, we could learn about the changes in the electrostatic potential (e.g., upon FGA).
• The two thin films (49, 62 Å – black and red traces) were found to be amorphous by XRD and XAS whereas the two thicker ones (76, 93 Å – blue and green traces) were tetragonal.
• The features in the 850-1000 cm\(^{-1}\) are common to all spectra suggesting that these features not related to the phase of the film.
• The frequencies of the two main features are \(~700\) and \(~750\) cm\(^{-1}\) in FTIR spectra. Also seen two bars (more intense than others in this frequency range) approximately at these two frequencies (\(~700\) and \(~750\) cm\(^{-1}\) ).