High resolution core level photoemission studies of high-k dielectric semiconductor interface formation

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Outline of talk

• Why high-k dielectrics?

• Issues associated with integration – control of interface layer

• High resolution photoemission study of interface formation between HfO$_2$ and MgO on ultrathin SiO$_x$ interlayer.

• CV measurements on MgO based MOS structures
HIGH-K MATERIALS: MOTIVATION
MOSFET dielectric replacement

65 nm (2007) MOSFET
[Source: INTEL]

$T_{ox} < \sim 2.5 \text{ nm} - \text{direct quantum mechanical tunneling}$
Importance of interface characterisation

Control of SiO\textsubscript{x} interface layer is critically important to device performance

\[
\text{EOT} = \left( \frac{3.9}{\kappa} \right) t_{hi - \kappa} + t_{SiO_x}
\]

= High-k layer + Interface layer

If you want to achieve EOT below 1nm, it is critical to control thickness of SiO\textsubscript{x} interface layer

- XPS
- Synchrotron radiation based photoemission
- TEM
- HAADF-STEM
Why MgO?

High chemical stability
Wide bandgap
Thermal stability
Possibility to form abrupt interfaces

<table>
<thead>
<tr>
<th>Material</th>
<th>k</th>
<th>Eg(eV)</th>
<th>CBO(eV)</th>
<th>VBO(eV)</th>
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<tbody>
<tr>
<td>SiO₂</td>
<td>3.9</td>
<td>9.0</td>
<td>3.2</td>
<td>4.7</td>
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<tr>
<td>Al₂O₃</td>
<td>9</td>
<td>8.8</td>
<td>2.8</td>
<td>4.9</td>
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<tr>
<td>MgO</td>
<td>10</td>
<td>7.8</td>
<td>3.4</td>
<td>3.3</td>
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<tr>
<td>HfO₂</td>
<td>25</td>
<td>5.8</td>
<td>1.4</td>
<td>3.3</td>
</tr>
</tbody>
</table>

Heats of Formation
MgO = -601.8 kJ/mol
SiO₂ = -859 kJ/mol
HfO₂ = -1113kJ/mol
Al₂O₃ = -1675kJ/mol
Integration issues for high-k materials

Mobility Degradation

Decreasing interlayer thickness reduces mobility in substrate

Locquet et al JAP 100 051610 (2006)

Leakage decreases by factor of 10 for every monolayer of SiO$_2$ at the interface - however EOT increases.

3nm HFO$_2$
EOT=1nm


Decreasing interlayer thickness reduces mobility in substrate
Mobility Degradation in High-\(k\) Gate MOSFETs

Both oxide charge and remote phonon scattering reduce as SiO\(_2\) interlayer thickness increases.

- Oxide charge
- Interface states
- Remote phonon
- Surface roughness
HfO$_2$ and MgO on silicon comparison study

- Grow ultra thin self limiting buffer oxide on silicon
- In situ deposition and characterisation of high-k layers
  (a) HfO$_2$ on ultra thin buffer oxide
  (b) MgO on ultra thin buffer oxide
- MgO on H-terminated silicon and CV characterisation on MOS structures
Interfacial buffer oxide - atomically abrupt

Silicon 2p Spectra
Ultra-thin Si-O on Si(111)

Estimated Oxide Thickness $d = 2.9\text{Å}$

$\Delta E$ (eV)

$+0.95$

$+1.01$

$+1.75$

$+1.85$

$+2.48$

$+2.62$

$+3.9$

$+3.55$

Exposing atomically clean Si(111) surface to molecular oxygen at 600°C.

Thermally grown self limiting ultrathin (0.3nm) SiO$_x$ layer

Sieger et al. PRL 77 2759 (1996)

FIG. 4. An abrupt interface model for SiO$_2$/Si(111). There are two possible terminations, as indicated in the figure. The oxidation states for Si atoms at and near the interface boundary are labeled.
**HfO$_2$/SiO$_x$ interface formation**

Thickness of interfacial oxide increases as HfO$_2$ is deposited at RT.
**MgO /SiOₓ interface formation**

Thickness of interfacial oxide increases as MgO is deposited. For both HfO₂ and MgO deposition saturation thickness of ~0.6-0.7nm. Original SiOₓ/Si interface has been disrupted at RT.
Capacitance – voltage measurements
MgO on Si

MOS capacitors fabricated by
E-beam deposition of MgO on HF etched Si
Ex-situ e-beam deposition of Pd contacts
Pattern defined by wet chemical lift-off process

Pd/MgO/Si MOS capacitor structures
Ambient degradation of MgO films

Heats of Formation
MgCO$_3$ = -1113 kJ/mol
Mg(OH)$_2$ = -924 kJ/mol
MgO = -601.8 kJ/mol

Rate of surface hydroxides and carbide growth
Capacitance for silicide gate process

MgO deposition on Si surface
In-situ Si deposition (100nm) cap
Ex-situ Ni deposition
500°C FUSI anneal

Exact scaling of $C_{\text{max}}$ with thickness
Low frequency dispersion
Low interface state densities

Suggests minimal interfacial layer
Si-H MgO interface formation

MgO deposition on H-terminated Si surface in ultra high vacuum

Evidence of magnesium-hydroxy-silicate formation at interface

CV measurements suggest k value higher than SiO₂
Conclusions

• Metal ion catalytic effect induces room temperature oxidation at high-k/Si interface.

• Ultrathin buffer oxide on Si is disrupted by dielectric deposition resulting in roughened interface – impact on mobility.

• Correct capacitance scaling with MgO thickness suggests minimal interfacial oxide layer.

• Photoemission analysis of the MgO/H-terminated Si interface shows the presence of a magnesium-hydroxy-silicate interfacial layer 0.5-0.6nm thick.
Acknowledgements


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