In situ low-angle x-ray scattering study of phase separation at initially mixed HfO₂-SiO₂ thin film interfaces

Paul C. McIntyre
Jeong-hee Ha

Department of Materials Science and Engineering
Stanford University, Stanford CA

Funding: Semiconductor Research Corporation Task 1016.001
Stanford Initiative in Nanoscale Materials and Processes

March 10, 2005
Motivation

Subsequent high temperature thermal processing causes **phase separation**


Metal oxide/SiO$_2$ interface structure uncertain due to deposition-induced mixing and thermal instability

Loss of desired dielectric and electrical properties

Need to investigate **effects of phase separation upon thermal process**

Need to understand **abruptness and stability of metal oxide/SiO$_2$ interfaces**
Phase separation of Hf-silicate films forms HfO$_2$/SiO$_2$ interfaces

- Initially intermixed HfO$_2$-SiO$_2$ alloy experiences a driving force for phase separation upon annealing

- Form regions of crystalline HfO$_2$ and amorphous SiO$_2$

Image courtesy of S. Stemmer

Growth of Metal Oxide Dielectrics: UV-Ozone Oxidation

- UV light supplies atomic oxygen and ozone to surface through the following reactions:
  \[
  \text{O}_2 + h\nu \rightarrow 2\text{O} \\
  \text{O} + \text{O}_2 \rightarrow \text{O}_3 \\
  \text{O}_3 + h\nu'' \rightarrow \text{O}_2 + \text{O}
  \]

- Benefits
  - Low temperature
  - Low contamination
  - Simplicity
  - Can modify substrate surface passivation

Multilayer test structure for HfO₂/SiO₂ interfaces

- (1.4nm SiO₂ / 4nm HfO₂)₄ structure on top of Si (100) substrate
- Grown by UVO oxidation

* Growth conditions
  - Hf, Si sputtered in 2 mTorr Ar pressure (~0.2 Å/sec) with base pressure 5E-9 Torr
  - Oxidized for 1 hr at 600 Torr O₂ pressure in UV light

* Advantage of using multilayers:
  - Deliberate exaggeration of particular interface effects
  - Separation of interface effects on electrical properties by comparing multi- and single layers

HfO₂-SiO₂ multilayer sample under study:
(by UV-Ozone Oxidation)

Courtesy of David Chi
X-ray diffraction: probe of local electron density

The scattered amplitude of the x-ray diffraction from the given system is just proportional to the Fourier transform of the local electron density:

\[
\rho_c(r) \propto \int e^{i \mathbf{q} \cdot \mathbf{r}} \rho_c(r) dV
\]

where:
- \(E_0\) : electric field magnitude
- \(r_e\) : electron radius
- \(R\) : distance from the sample to the detector
- \(q\) : scattering vector
- \(\rho_c(r)\) : spatial electron density distribution

So, we can deduce information about changes in the electron density distribution (e.g. a composition profile) by observing XRD data.
Multilayer structure and its XRD pattern

- Electron density distribution in the multilayer sample can be modeled as a square wave.
- The scattered amplitude is proportional to the Fourier series of the square wave given.
- The weighting of the $n=1$ (first order) harmonic wave reflects the degree of the interdiffusion.

$$\tilde{D} \equiv \frac{-L^2}{8\pi^2} \frac{d}{dt} \ln \left[ \frac{I(t)}{I(0)} \right]$$

\[\tilde{D} \quad \text{: effective interdiffusivity} \]

L \quad \text{: bilayer period}

I \quad \text{: the first-order low-angle x-ray modulation peak}
The scattered intensity for N layers is given by:

\[
I \propto \left( \sum_{n=0}^{N-1} f_n(q)e^{iqR_n} \right)^2 = f^2(q) \frac{\sin^2(Nq_zL/2)}{\sin^2(q_zL/2)}
\]

Measured data agree well with the simulated result:

Low angle XRD data

for (SiO₂/HfO₂)₄ multilayer structure
(HfO$_2$/SiO$_2$)$^4$ structure, N$_2$ anneal

The intensity of $n = 1$ satellite peak *increases* as annealing proceeds.

Evidence of phase separation at the initially-intermixed as-deposited HfO$_2$/SiO$_2$ interfaces.

**In-situ low-angle XRD**
(HfO_2/SiO_2)*4 structure, N_2 anneal

\[ \tilde{D} = -\frac{L^2}{8\pi^2} \frac{d}{dt} \ln \left[ \frac{I(t)}{I(0)} \right] \]

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Interdiffusivity (m^2/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>680.0</td>
<td>2.34*10^{-24}</td>
</tr>
<tr>
<td>713.3</td>
<td>5.65*10^{-24}</td>
</tr>
<tr>
<td>731.0</td>
<td>9.11*10^{-24}</td>
</tr>
<tr>
<td>752.0</td>
<td>25.18*10^{-24}</td>
</tr>
</tbody>
</table>

In-situ low-angle XRD
The activation energy $\Delta H$ for phase separation can be obtained from the Arrhenius rate law:

$$D_e = D_o \exp\left(-\frac{\Delta H}{k_BT}\right)$$

- The obtained $\Delta H$ for the phase separation is $2.06 \pm 0.15$ eV.


Summary

Accomplishments

- Used multilayer x-ray scattering to probe the kinetics of phase separation at as-deposited mixed HfO$_2$/SiO$_2$ interfaces
- Obtained the activation energy of $2.06 \pm 0.15$ eV for phase separation in HfO$_2$/SiO$_2$ interface system
- Determined temperature range for phase separation at initially-intermixed HfO$_2$/SiO$_2$ interface: $T > 650^\circ$C