Scanning Transmission Electron Microscopy of Thin Oxides

Susanne Stemmer

Materials Department
University of California Santa Barbara

Collaborators:
- Z. Chen, Y. Yang, D. Klenov (UCSB)
- W. J. Zhu, T.P. Ma (Yale)
- S. Ramanathan, P. McIntyre (Stanford)
- D. Niu, G. Parsons (NCSU)
- J.-P. Maria, A. I. Kingon (NCSU)
- P. Lysaght, B. Foran (Sematech)
- C. G. Levi (UCSB)
- J. Gisby (NPL, UK)

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Scaling the gate oxide

- The functionality of a CMOS transistor is based on a very thin SiO₂ layer - the **gate oxide**
- Moore’s law: the number of components per chip doubles every 18 months (the same applies for the processing speed)
- SiO₂ becomes an unreliable insulator at ~ 1 nm thickness
- Potential Solution: replace SiO₂ with a material with higher dielectric constant and greater physical thickness:

\[ C = \frac{\kappa \cdot \varepsilon_0 \cdot A}{d} \]

Scaling the Gate Oxide

- Many oxides have a greater dielectric constant than SiO₂ (κ=3.9)
- However, few oxides are stable in contact with Si:
  - ZrO₂, HfO₂, Y₂O₃, La₂O₃,…
  - Silicates
  - Aluminates

Elements that have an oxide that is predicted to be stable in contact with Si

Schlom and Haeni, MRS Bulletin 27, March 2002
Issues in Scaling the gate oxide

- Dielectric constant
- Interface layers (SiO₂) reduce the capacitance density
- Stability, for example against reactions, interface oxidation
- Interface quality for high mobility in channel
- High-k structure and chemistry:
  - Crystallinity
  - Defects
  - Nonstoichiometry
- Band offsets with silicon: barrier heights for charge carriers need to be sufficiently high

ZrO₂ gate dielectric on Si
Conventional High Resolution Transmission Electron Microscopy (HRTEM) Image
Interface Stability of High-κ Dielectrics

As-deposited film:
- Low leakage and low EOT
- Amorphous
- Thin interfacial SiO₂ layer

Annealed film (700 °C/N₂):
- Leaky, increased EOT
- Partially crystallized
- Thicker interfacial SiO₂ layer

Hf-aluminate films grown at RT by jet-vapor deposition (T.P.Ma, Yale U.) w. 6.8 at% Al

- Need high-resolution structural, electronic and chemical information to explain changes in the dielectric/electrical properties
- Layers are thin (~ 2 - 4 nm)
- Atomic resolution EELS
Scanning Transmission Electron Microscopy

- TEM/STEM: JEOL 2010F with field-emitter and Gatan imaging filter
- Probe size used for EELS: 0.2 nm

Conventional high-resolution TEM

Annular dark-field image

Structural and analytical information of a-priori unknown structures can be obtained in parallel and with atomic spatial resolution
Electron Energy Loss Spectroscopy - Near Edge Fine-Structures (ELNES)

The “fine-structure” of EELS core loss edges (ELNES) represents the unoccupied density of states just above the Fermi level.

\[ J(E) \propto |M(E)|^2 N(E) \]

- Can be used to “fingerprint” bonding information
- Information similar to X-ray absorption spectroscopy (XANES)
Characteristic double-peaks at O K-edge onsets: reflect unoccupied metal $d$-states (via $p$-$d$ hybridization)

$d$-states determine conduction band offset with silicon

Splitting present in amorphous films
- Represent Hf-O nearest neighbor configuration
- Indicate of good oxygen stoichiometry
- Device processing conditions/atomic rearrangements changes electronic structure of high-$k$
High-$k$ stability at 1000 °C?

**Excess oxygen ⇔ reducing conditions**

- Under reducing conditions, such as the poly-Si electrode depositions, silicide formation is observed.

ZrO$_2$ film after poly-Si deposition and 10 sec/1025 °C anneal
Gutowski et al. APL 80 (2002) p. 1897
Low oxygen partial pressures (< 10^{-4} torr) can preserve a thin (< 1 nm) interfacial SiO$_2$
Silicide formation at low $p_{O_2}$ (~ $10^{-7}$ torr)

- At $10^{-7}$ torr / 1000°C, the reaction
  
  \[ 2\text{Si}(s) + O_2 (g) \rightarrow 2\text{SiO}(g) \]

  is favored.

- The relevant reaction is then
  
  \[ 2\text{Si} + \text{ZrO}_2 \rightarrow \text{ZrSi}_2 + O_2 (g) \]

  [Note: the sum of the above two reactions is:
  
  \[ 4\text{Si}+\text{ZrO}_2\rightarrow\text{ZrSi}_2+2\text{SiO}(g) \]]

- The equilibrium partial pressure of this reaction is $3.28 \times 10^{-29}$ torr

- $\text{ZrSi}_2$ should not form
Nonstoichiometry and Silicide Reaction

- However, thin films are highly nonstoichiometric and unlikely to be at equilibrium.
- The free energy change of this reaction and the driving force depend on the concentration of vacancies.

\[
\Delta G^\circ_{\text{tot}} = -RT \ln K
\]

\[
\Delta G^\circ_{\text{tot}} = -RT \ln \left( \frac{1}{16 [V_\circ^{\bullet\bullet}]^6} \right)
\]

with \([e^\bullet] = 2[V_\circ^{\bullet\bullet}]\)

- The equilibrium vacancy concentration is \(~ 0.3\%\) at 1473K.
- For any nonstoichiometry greater than ZrO\(_{1.997}\) the silicide reaction will proceed.

\[
\text{ZrO}_2 + 4e^\bullet + 2V_\circ^{\bullet\bullet} + 2\text{Si} \rightarrow \text{ZrSi}_2 + 2O_\circ^x \quad \Delta G^\circ_{\text{tot}} = -390 \text{kJ/mol}
\]
High-$k$ stability at 1000 °C?

**Excess oxygen (cont’d)**

- Can *in-situ* capping prevent interfacial SiO$_2$ growth?
- How about silicate reactions?
- Example: Y$_2$O$_3$
  - SiO$_2$+Y$_2$O$_3$ $\rightarrow$ Y$_2$SiO$_5$ $\Delta$H=$\text{-}52$ kJ/mol
    
    *Fabrichnaya et al. Z. Metallk. 92, 1083 (2001)*
  - In presence of excess oxygen, silicate should form

$Y_2O_3$ grown by remote oxygen plasma assisted CVD on Si ($T_{\text{sub}} = 350 – 450$ °C)
G. Parsons, D. Niu (NCSU)
**In-situ** Si capped CVD Y$_2$O$_3$ films

- *In-situ* capped films have only an extremely thin (< 0.5 nm) interface SiO$_2$ layer
- Silicate reaction with poly-Si and Si substrate interfaces, nitridation impedes the substrate reaction.
Silicate Formation During High-T Anneals

- $\text{Y}_2\text{O}_3$ strongly absorbs and reacts with water
- OH or excess O might be present in low-T CVD process
- Extreme case:
  \[
  2\text{Y(OH)}_3 + 1.5\text{Si} \rightarrow \text{Y}_2\text{O}_3 + 1.5\text{SiO}_2 + 1.5\text{H}_2
  \]
- However, $\text{Y}_2\text{O}_3$ and $\text{SiO}_2$ are unstable with respect to silicate formation:
  \[
  \text{Y}_2\text{O}_2 + 1.5\text{SiO}_2 \rightarrow \text{Y}_2\text{SiO}_5 + 0.5\text{SiO}_2
  \]
- This should give a 1.4 nm thick $\text{SiO}_2$ for a 6 nm silicate film, but:
  \[
  0.5\text{Y}_2\text{SiO}_5 + 0.5\text{SiO}_2 \rightarrow 0.5\text{Y}_2\text{Si}_2\text{O}_7
  \]
- $\text{SiO}_2$ should only form if
  - there is enough O in the annealing atmosphere or
  - the silicate reaction is kinetically limited.
- Conditions are met for uncapped or *ex-situ* capped films, but not for *in-situ* capped films.
- Silicate reaction requires excess O: present in CVD process/film?
High-\(k\) stability at 1000 °C?

2. Phase separation of the silicates

Why use silicates?

- Increase crystallization temperatures
- Greater resistance to oxygen diffusion

Experiment: CVD Hf-silicates (AMAT) with different compositions annealed at 1000 °C/10 sec
Phase separation: Hf- and Zr-silicates

- HfO$_2$-SiO$_2$ with different compositions after 1000 °C/10 sec anneal
- The volume fraction of crystalline phase is proportional to the amount of HfO$_2$.
- The crystallizing phase is always monoclinic HfO$_2$, embedded in an amorphous silica-rich phase (very similar microstructures)
However, the situation is more complicated in ZrO$_2$-SiO$_2$ and, likely the HfO$_2$-SiO$_2$ system, due to presence of the liquid miscibility gap and spinodal.

Compositions within the metastable extensions of the spinodal will phase separate below the glass transition temperature and then crystallize.

Compositions outside the metastable extensions of the liquid miscibility gap will nucleate crystalline HfO$_2$ above the glass transition temperature.

Experimentally observed grain sizes are not very different, likely due to the large undercooling.
Calculated metastable extensions of the liquid miscibility gap in ZrO$_2$-SiO$_2$

Thermodynamic calculations of the metastable extensions of the miscibility gap by J. Gisby and R. Taylor:

At 1000 °C, compositions between 40% and 90-95% lie **inside** the spinodal. They will spontaneously phase separate.

Required device annealing temperature (1000 °C)
Summary

- High-spatial resolution EELS and HRTEM was essential to show:
  - A processing window exists for ZrO$_2$/Si films between interface SiO$_2$ growth and silicide formation
  - Oxygen deficiency responsible for silicide reactions
  - Excess oxygen in low temperature CVD process causes silicate formation in Y$_2$O$_3$/Si system
  - Nonstoichiometry (and how to measure it) is an important issue in thin dielectric films
- Phase separation in Hf-silicate and Zr-silicate systems with different composition has different pathways, but resulting microstructures look similar at large undercoolings
- There are a great number of stability problems that need to be solved for high-$\kappa$'s.