Growth of $\text{Y}_2\text{O}_3$ and $\text{HfO}_2$ as Single Compounds and as Nanolaminates on Si using Atomic Layer Deposition

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Motivation for Research

• To work with new high dielectric constant (k) materials such as HfO$_2$ and Y$_2$O$_3$ to replace SiO$_2$ in micro- and nano-electronics

• To run experiments in the atomic layer deposition (ALD) reactor and to examine thin film growth rates

• To analyze the resulting thin films on silicon using spectral ellipsometry, Fourier Transform Infrared (FTIR) spectroscopy, X-ray Photoelectron Spectroscopy (XPS), and Atomic Force Microscopy (AFM).
Hypotheses

- A self-limiting reaction between an yttrium precursor, a hafnium precursor, an oxidizer, and the silicon substrate

- Good film uniformity on the substrate (using a spectral ellipsometer)

- Absence of organic compounds in the resulting film structures (using FTIR spectroscopy)

- Stoichiometry of the high-k material and the bonding states of the elements (using XP Spectroscopy)
New High-k Dielectric Materials

- Last summer and through the following school year work was conducted with Hafnium and Yttrium
  
- Hafnium oxide has a k value of 20-25
  
- Yttrium oxide has a k value of 15-18
Why co-deposition?

- Enhances dielectric constant
- Aids in the size minimization of semiconductor devices
Atomic Layer Deposition (ALD)

- Uses pulses of gaseous reactants (precursor and oxidizer) alternately fed into the reactor
- Produces atomic control
- Film thickness depends on number of deposition cycles
ALD Process

- “One Cycle”
- Precursor
- Purge (N$_2$)
- Oxidizer (H$_2$O)
- Purge (N$_2$)

http://www.cambridgetech.com/
Acceptable Temperature Window

- ALD reactions usually occur between 200-400 °C in the reactor
- Above 400 °C, the chemical bonds are not stable and the precursor may decompose
- Below 200 °C, the reaction rate may be reduced

[Diagram showing the acceptable temperature window]
Properties of the Precursors

- $\text{Y(CpCH}_2\text{CH}_3\text{)}_3$ -- tris(ethylcyclopentadienyl) yttrium
  - Vapor pressure: $\sim 60$ mTorr @ $100 \degree C$
  - Decomposition temperature: $> 350 \degree C$
  - Melting point: $38 \degree C$
- Hf[N(C₂H₅)₂]₄ -- tetrakis(diethylamino)hafnium
  - Boiling point: 130°C
  - Density: 1.22g/ml
  - Appearance: dark yellow liquid

Experimental Conditions

- ALD Reactor
  - Precursor A (Hafnium): 65 °C
  - Precursor B (Yttrium): 120 °C
  - Reactor: 250 °C

$Y_2O_3$ Growth Rate vs. Precursor Dosage

Y$_2$O$_3$ Growth Rate vs. Reactor Temperature

XP Spectra of $Y_2O_3$ on Si

Quantification Results

Y Atomic Concentration %: 39.2
O Atomic Concentration %: 60.8

O:Y = 60.8/39.2 = 1.5

Therefore $Y_2O_3$ was produced on the substrate.
Surface Morphology (AFM)

rms roughness ~.4 nm which is below 1% film thickness

HfO$_2$ Growth Rate vs. Precursor Dosage

Growth rate (Å/cycles) vs. Number of precursor pulses per ALD cycle.
HfO$_2$ Growth Rate vs. Purge Time

Growth rates (Å/cycles) vs. Purge time after moisture pulse (s)
HfO$_2$ and Y$_2$O$_3$ Growth Rate vs. Reactor Temperature

Growth rates (Å/cycles) vs. Reactor temperature (°C)

Overlap (250-285 °C)

Y$_2$O$_3$ ALD window

HfO$_2$ ALD window

- HfO$_2$
- Y$_2$O$_3$
Low Temperature Deposition of HfO$_2$

- Joint effort to deposit Hafnium Oxide onto polymer nanofibers
  - Nanotubes
  - Physical properties ...compression
  - Electrochemical properties

- Low temperature needed to prevent vaporization
  - below 60 °C
**HfO$_2$ Average Thickness**

After 50 cycles

![Graph showing the average thickness of HfO$_2$ after 50 cycles as a function of reactor temperature.](image)
Hurdles

- Lower temperature needed to prevent vaporization
  - Room temperature not controllable
- Try 30 °C
- Fibers getting broken apart - substrate placement in the reactor
  - Slow change in air pressure and purging reduces fiber movement
  - Substrate holder moved away from reactor feed to reduce purge pressure coming from manifold
Cross Section of Reactor

All measurements and temperatures are the same as in previous slide
Findings

- Placement of fibers in the back of the vacuum chamber did not produce any encouraging results

- Fluid dynamics were changed

- Grated metal sheets were tried

- Ended up with steel envelope
Future Work

• Analysis of samples using FT-IR to determine composition of deposition

• Teaching module / all school lab
different classes have different inquiries
References


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