ALD ZrO$_2$ and HfO$_2$: Processing Aspects and Dielectric Behavior

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Investigate of phase stability in high-k dielectric system by thermodynamic analysis

$\text{ZrO}_2 / \text{HfO}_2$

+ ALD (Atomic Layer Deposition) technique for high quality thin film

1) Study ALD processing fundamentals for high-k materials
2) Investigate alternate precursors to metal halides ALD; assess precursor utilization efficiency, ESH / dielectric performance trade-offs
3) Investigate selective ALD (w/ Bent, Muscat, Musgrave groups)
Demand for High-k Materials

High leakage current due to direct tunneling

Solution: Replace SiO$_2$ with high-k dielectric to increase physical thickness

Thermodynamically possible candidates: ZrO$_2$, HfO$_2$, Al$_2$O$_3$, Zr-silicate, Hf-silicate

$C_{ox} = \varepsilon_{ox} \varepsilon_0 A / t$

To maximize $C_{ox}$, decrease $t_{ox}$ or increase $\varepsilon$.
ALD (Atomic Layer Deposition) CVD

- **Surface saturation controlled process**
- **Layer-by-layer deposition process**
- **Excellent film quality and step coverage**

ZrCl₄(ad.) + 2H₂O(g) → ZrO₂(s) + 4HCl(g)
Schematic Diagram of ALD System

- Cold wall and resistive heating type ALD system
- Load-lock system and high vacuum chamber
- Solid (ZrCl$_4$/HfCl$_4$) and liquid source (H$_2$O) delivery system installed for individual and nanolaminate structure experiments
- Computer controlled ALD processing
**Process Conditions of ALD Process**

- **Reactant A** (ZrCl₄/HfCl₄)
  - 60 sec
  - 30 sec
  - Pulse: 1~2 sec
  - Purge
  - 1 cycle
  - Time (sec)

- **Reactant B** (H₂O)
  - 1 cycle
  - Time (sec)

- **Base pressure** = ~10⁻⁸ Torr
- **Process temperature**: 250°C / 300°C.
- **Process pressure**: 0.5 Torr
- **Source temperature**: H₂O (liquid) = 20°C.
  - ZrCl₄/HfCl₄ (Solid) = 150°C
Chemical Utilization of ALCVD ZrO$_2$ Process

- Basic parameters (Based on current research ALD system)
  
  - $A$ (area of wafer), $\rho$ (density of ZrO$_2$) = $3.02 \times 10^{22}$ (#/cm$^3$)
  - $r$ (growth rate) = 0.52 (Å/cycle) (M. Ritala, Appl. Surf. Sci., 75, p333, 1994)
  - $p$ (vapor pressure of ZrCl$_4$ at 150°C) = 64 (mTorr)
  - $v$ (flow rate of N$_2$ carrier) = 20 (sccm)

- Total number of molecules deposited
  
  $$N_{\text{DEP}} = A \times r \times \rho = 7.16 \times 10^{15}$$ (#/cycle) = $7.16 \times 10^{15}$ (#/sec) (for 1sec pulsing)

- Total number of molecules used for ALD process
  
  $$N_{\text{FLOW}} = N_A \times pv/RT = 4.85 \times 10^{20}$$ (#/sec)

- Chemical utilization factor
  
  $$F = \frac{N_{\text{DEP}}}{N_{\text{FLOW}}} \sim 1.5 \times 10^{-5}$$ : for 3 in wafer
  
  $$\sim 2.4 \times 10^{-4}$$ : for 12 in wafer

- This can be increased by decreasing flow rate of precursor through more efficient chamber design
Growth Kinetics of ALD ZrO$_2$ Process

- Typical linear growth rate: ~0.06 nm/cycle.
- Independent of H$_2$O pulsing time.
- Excellent uniformity: < 0.1nm across 3” wafer.
- Growth is insensitive to ZrCl$_4$ pulsing time and flow rate: signature of ALD process.
Effect of H$_2$O Flow on Growth Rate & Uniformity

- Growth rate is linearly dependent on H$_2$O flow rate.
- Uniformity is primary affected by the sufficient dosing of H$_2$O in HfO$_2$ process.
I-V Characteristics of ALD ZrO$_2$ with Thickness

- ZrO$_2$ film was grown on chem. oxide surface w/o HF strip
- Films were deposited at 250°C with various thickness.
Leakage Current Mechanism of ALD ZrO$_2$ on Chemical Oxide

- Thick oxide is more sensitive to temperature.
- Thick oxide shows high temp. dependence at low field region and low temp. dependence at high field region.
Leakage Current Mechanism of ALD ZrO$_2$ on Chemical Oxide

- Temperature dependency of thick ZrO$_2$ oxide follows the trap-assisted tunneling model” (M. Houssa et al., JAP 87, 8615 (2000))

- High number of bulk traps might originate from high concentration of chlorine or defects due to the low temperature deposition. : large hysteresis (? V~230mV) from CV measurement, which corresponds to $N_{\text{trap}} = \sim 2.3 \times 10^{12}$ (cm$^{-2}$)

Pt gate electrode
C-V Characteristics of ALD ZrO$_2$ on Chemical Oxide

- Series Pt electrode/ZrO$_2$/p-Si/Backside Al structure.
- Resistance was numerically corrected using two different frequency measurements (K.J.Yang et al., IEEE Elec. Dev. Lett. 66, 1500, 1999).
- Thinner sample shows less hysteresis.
- Preliminary electrical results in keeping with data from state-of-the-art ALD gate dielectrics (C.M. Perkins et al., Appl. Phys. Lett. 78, 2357, 2001)
C-V & IV Characteristics of ALD HfO$_2$ on Chemical Oxide

- First ALD HfO$_2$ sample shows good C-V curve shape and low leakage current (EOT=1.8 nm @ -2V on chemical oxide).
Microstructure of As-grown ALD ZrO$_2$

- ZrO$_2$ film was grown on chemical oxide surface w/o HF strip.
- Film deposited at 250°C contains mainly polycrystalline ZrO$_2$.
- Indexing of TEM diffraction pattern reveals Tetragonal ZrO$_2$.
- Interface and surface roughness obtained from TEM and AFM are encouraging.
Microstructure of As-grown ALD HfO$_2$

- HfO$_2$ film was grown on chemical oxide surface w/o HF strip.
- Film deposited at 250°C are *amorphous* according to HRTEM image and electron diffraction.
- Interface and surface roughness obtained are also encouraging.
Future Experimental Plan

- **Building ALCVD system**
- **Set-up & optimization of ZrO₂ process condition w/ ZrCl₄**
- **Set-up & optimization of HfO₂ process condition w/ HfCl₄**
- **Experiments (w/Bent group) on Si (100) surface prep. for selective deactivation of ALD**
- **Set-up & optimization of MO₂ process condition w/ metalorganic precursor**
- **Assess chemical utilization & waste generation for both MCl₄ and metalorganic precursor processes**

**Current Status**