ALD ZrO_2 and HfO_2: Processing Aspects and Dielectric Behavior

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Project Objectives

Demand for high-k dielectric material
& metal electrode for sub 0.1❍m transistor

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

ZrO_2 / 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)

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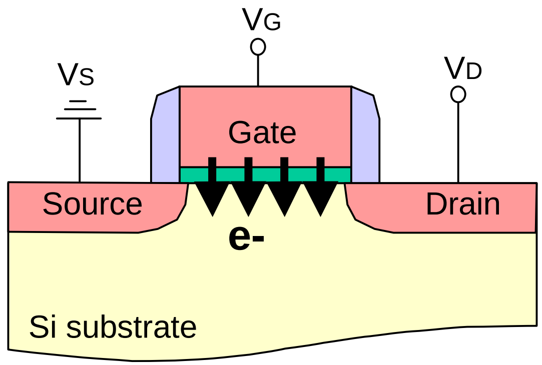
Demand for High-k Materials



High device density & high speed transistor need high gate oxide capacitance and gate oxide scaling

$C_{ox} = e_{ox} e_o A / t$

To maximize C_{ox}, decrease t_{ox} or increase e

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_2O_3, Zr-silicate, Hf-silicate

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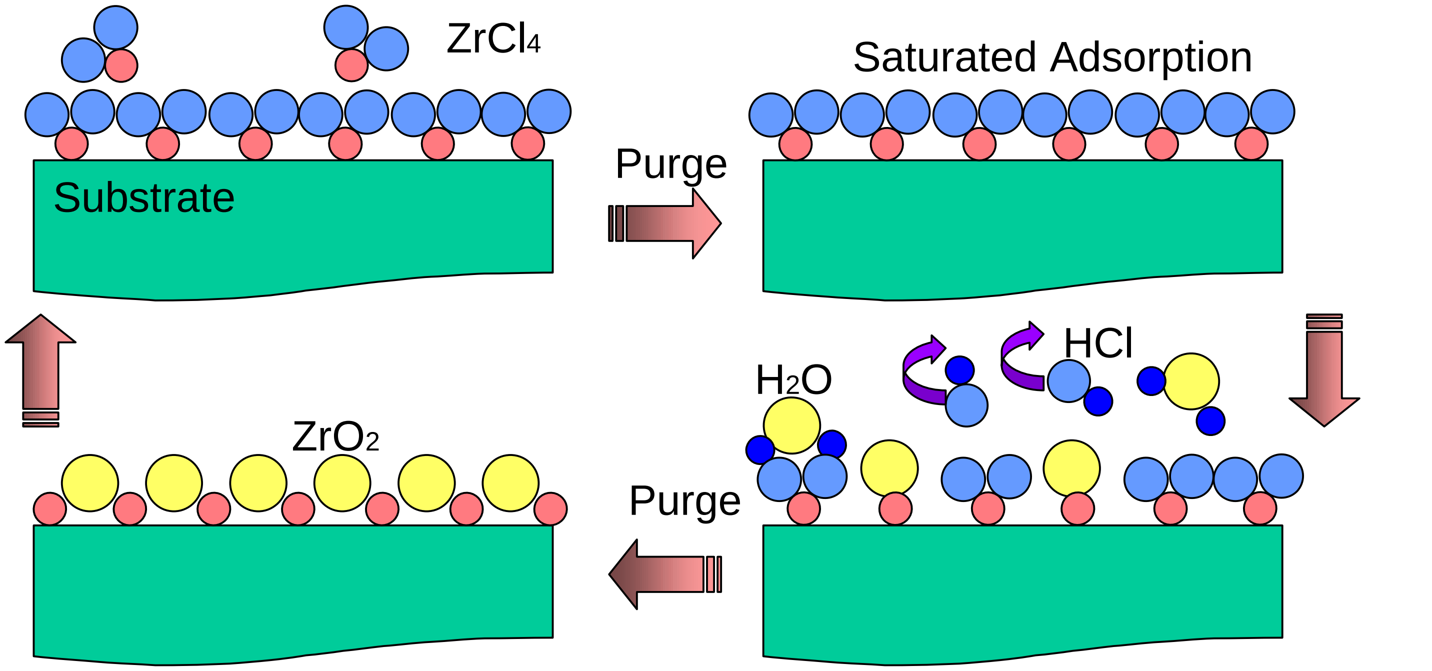
ALD(Atomic Layer Deposition) CVD



$ZrCl_4(ad.) + 2H_2O(g) \rightarrow ZrO_2(s) + 4HCl(g)$

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

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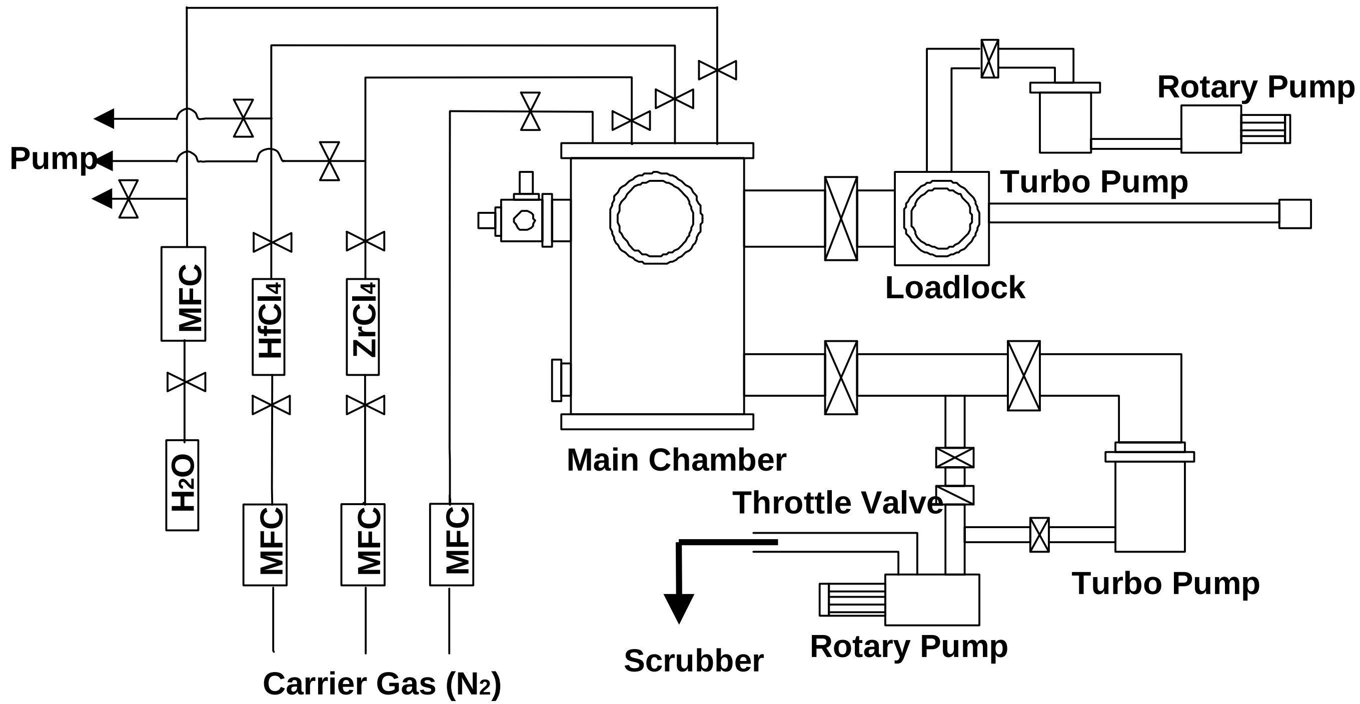
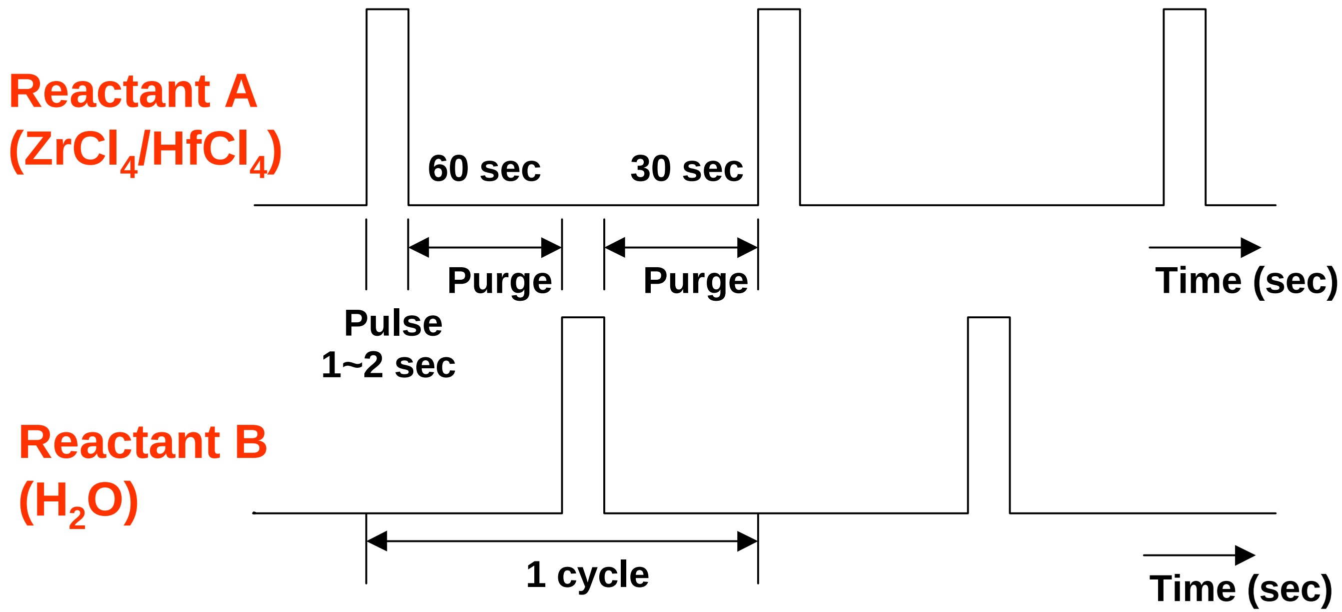
Schematic Diagram of ALD System



- Cold wall and resistive heating type ALD system
- Load-lock system and high vacuum chamber
- Solid ($ZrCl_4$/$HfCl_4$) and liquid source (H_2O) delivery system inst alled for individual and nanolaminate structure experiments
- Computer controlled ALD processing

Process Conditions of ALD Process



- Base pressure = ~10^{-8} Torr
- Process temperature : 250°C /300°C.
- Process pressure : 0.5 Torr
- Source temperature : H_2O (liquid) = 20°C.
  $ZrCl_4/HfCl_4$ (Solid) = 150°C

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Chemical Utilization of ALCVD ZrO_2 Process

- Basic parameters (Based on current research ALD system)

A (area of wafer), ρ (density of ZrO_2) = 3.02×10^{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

$N_{DEP} = A \times r \times \rho = 7.16 \times 10^{15}$ (#/cycle) = 7.16×10^{15} (#/sec) (for 1sec pulsing)

- Total number of molecules used for ALD process

$N_{FLOW} = N_A \times pv/RT = 4.85 \times 10^{20}$ (#/sec)

- Chemical utilization factor

$F = N_{DEP} / N_{FLOW} \sim 1.5 \times 10^{-5}$: 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

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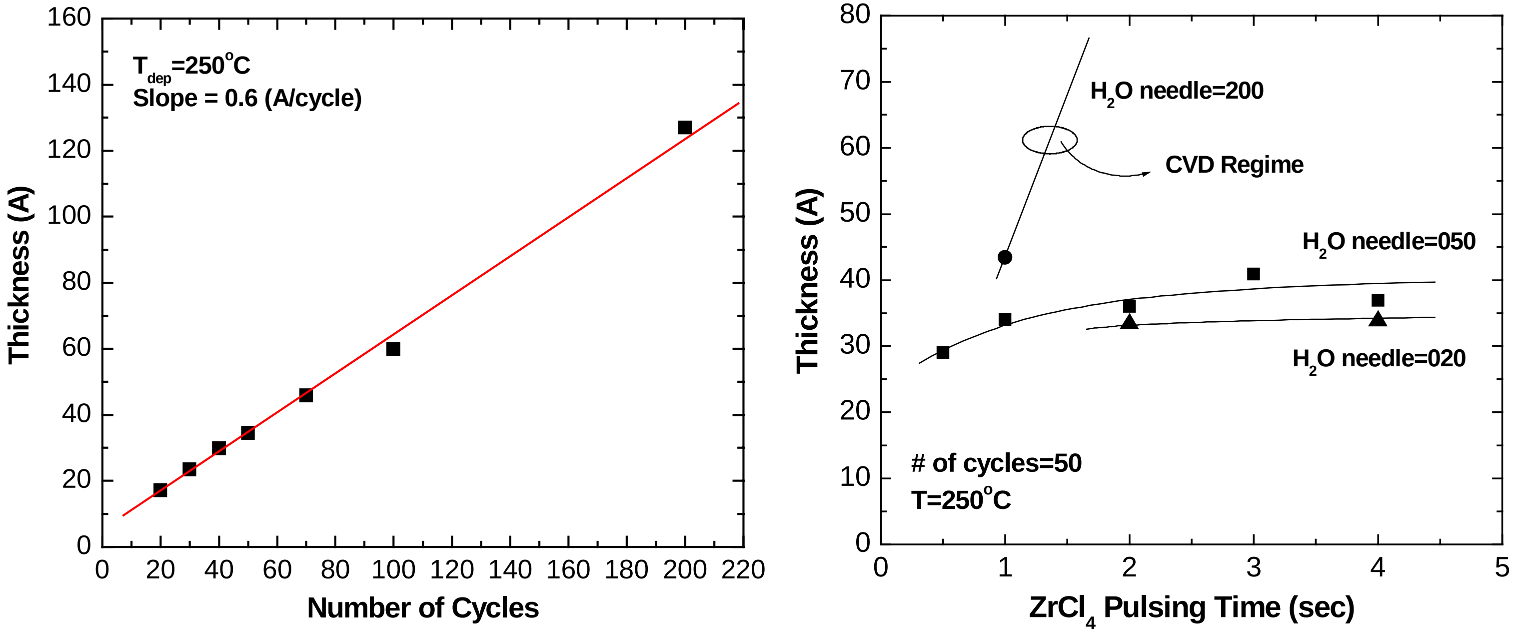
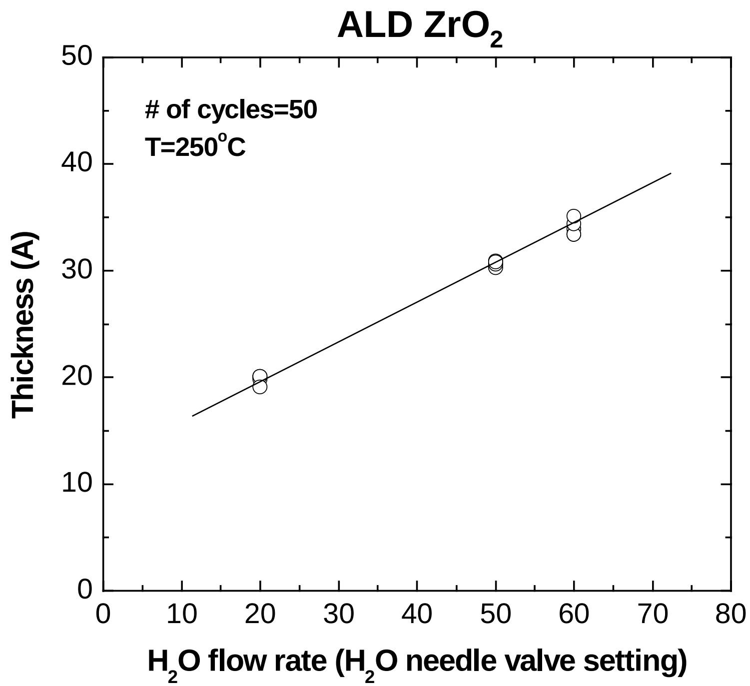
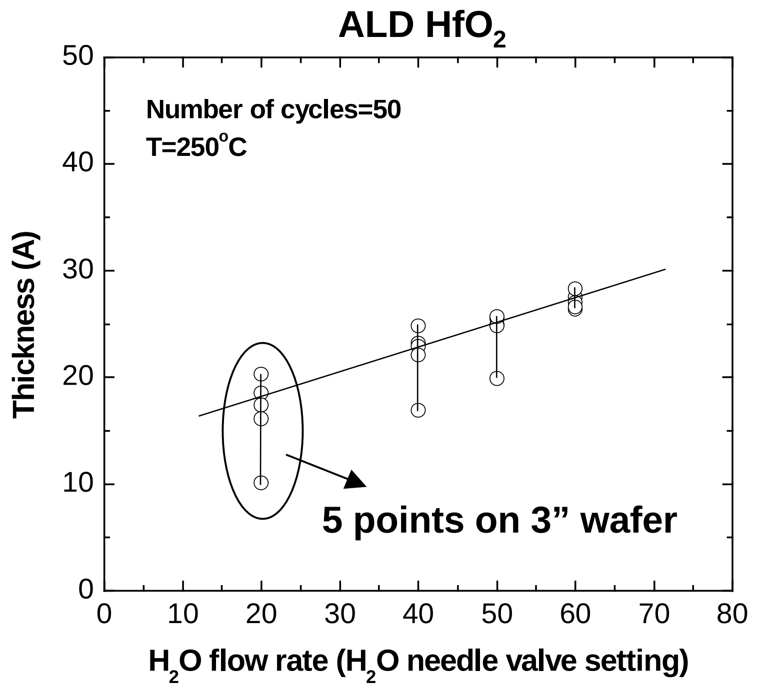
Growth Kinetics of ALD ZrO_2 Process



- Typical linear growth rate : ~0.06 nm/cycle.
- Independent of H_2O pulsing time.
- Excellent uniformity : < 0.1nm across 3" wafer.
- Growth is insensitive to $ZrCl_4$ pulsing time and flow rate : signature of ALD process.

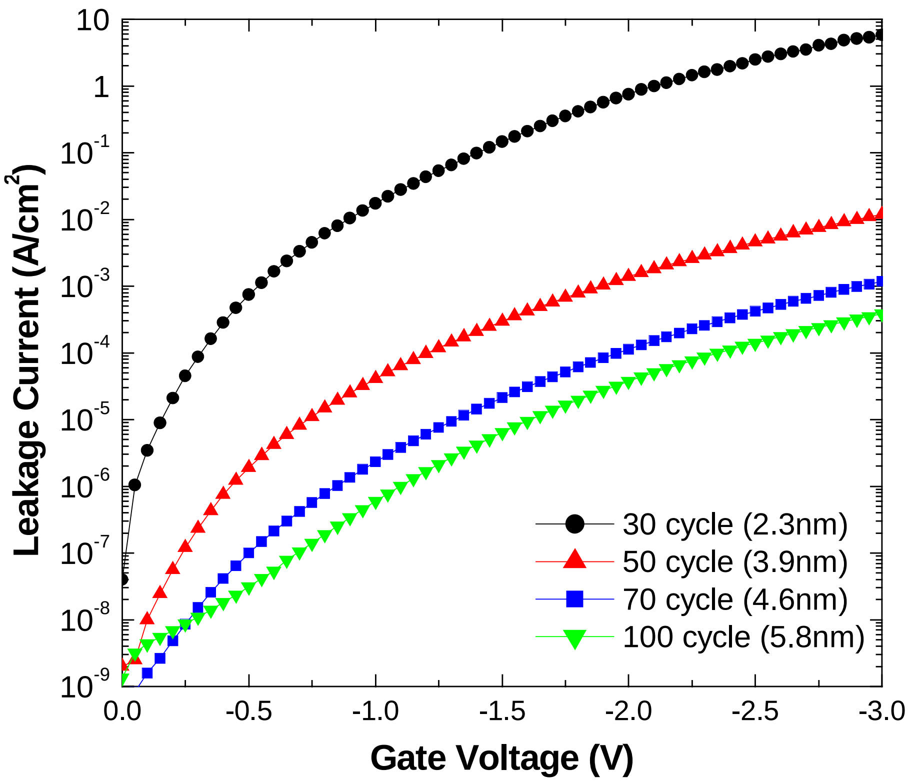
Effect of H_2O Flow on Growth Rate & Uniformity





- Growth rate is linearly dependent on H_2O flow rate.
- Uniformity is primary affected by the sufficient dosing of H_2O 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.

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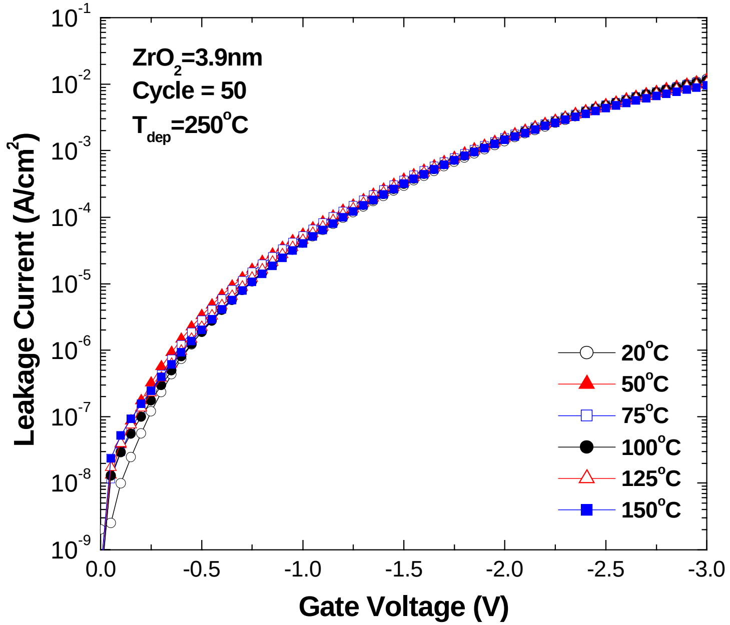
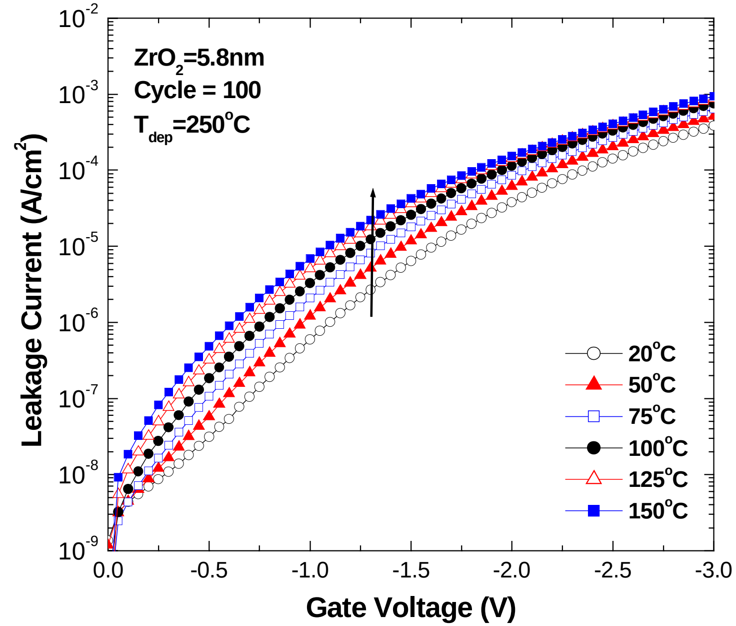
Leakage Current Mechanism of ALD ZrO_2 on Chemical Oxide





- 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.

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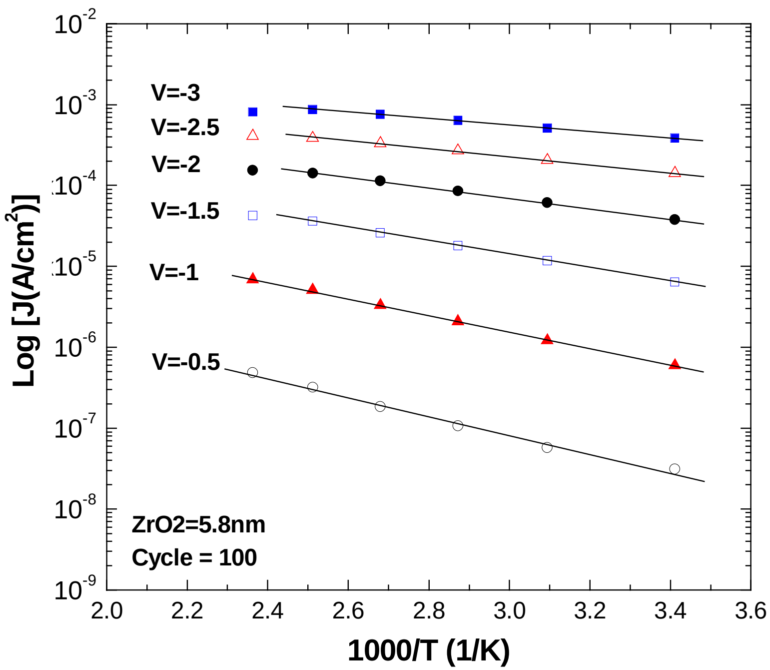

Pt gate electrode

- 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_{trap}=~2.3x10^{12} (cm^{-2})

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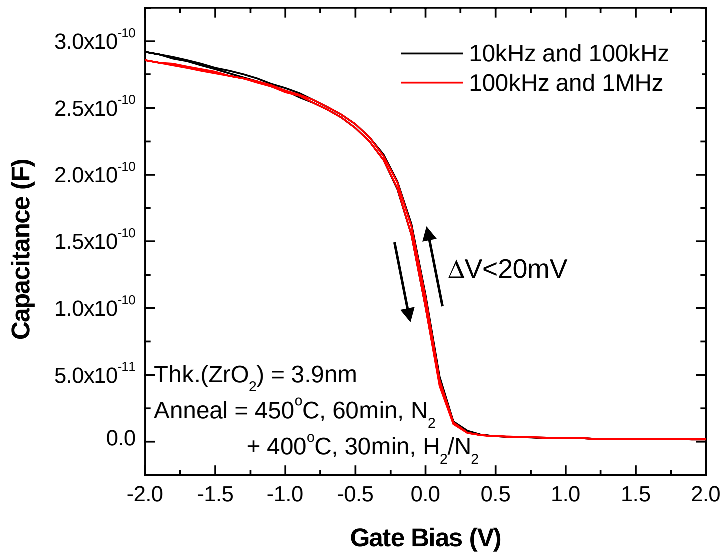
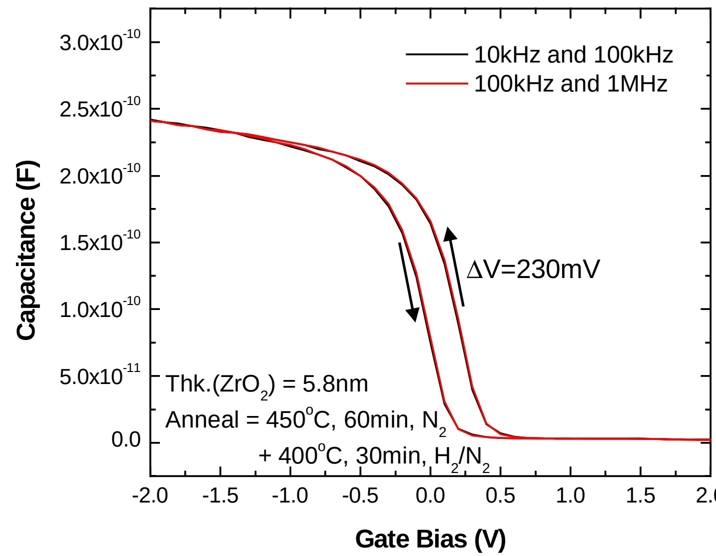
C-V Characteristics of ALD ZrO_2 on Chemical Oxide





- **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)**

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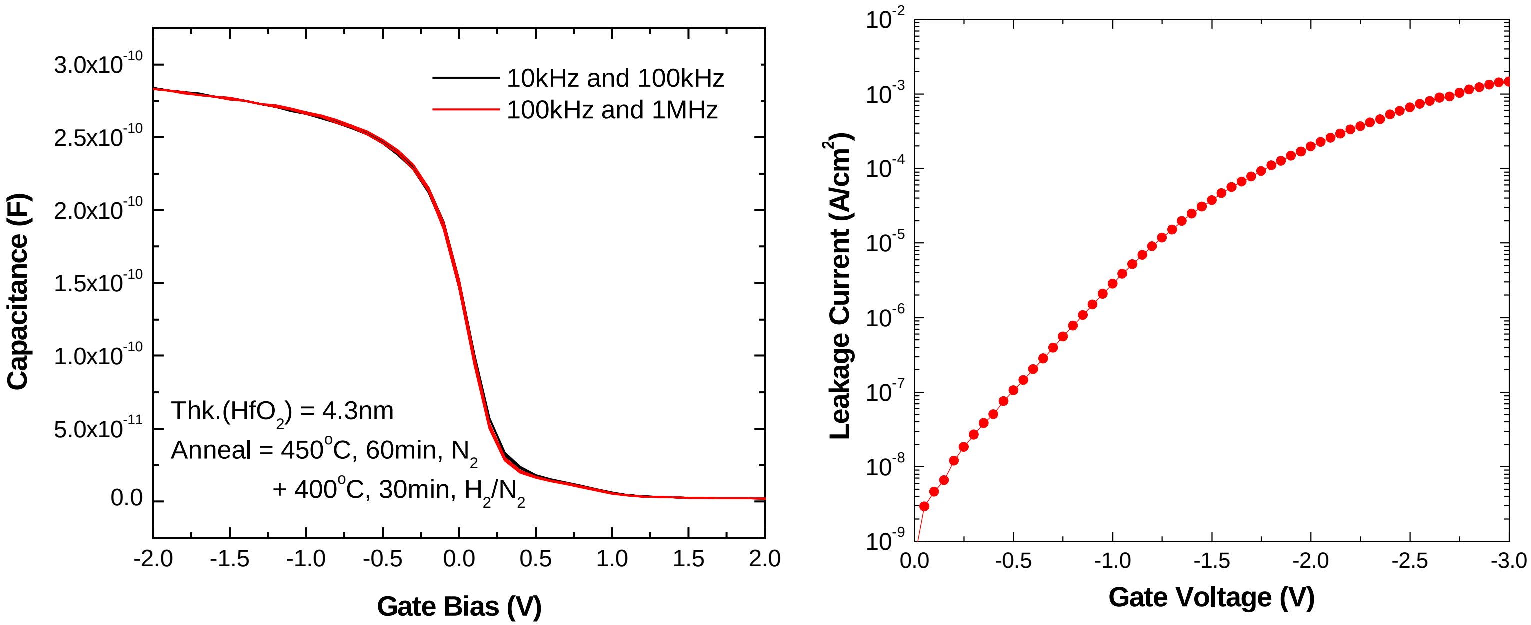
C-V & IV Characteristics of ALD HfO_2 on Chemical Oxide



- First ALD HfO_2 sample shows good C-V curve shape and low leakage current (EOT=1.8 nm @-2V on chemical oxide).

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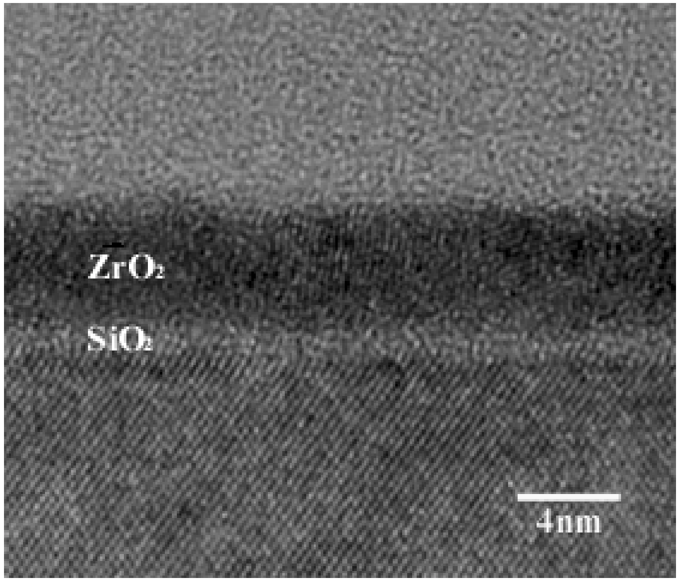
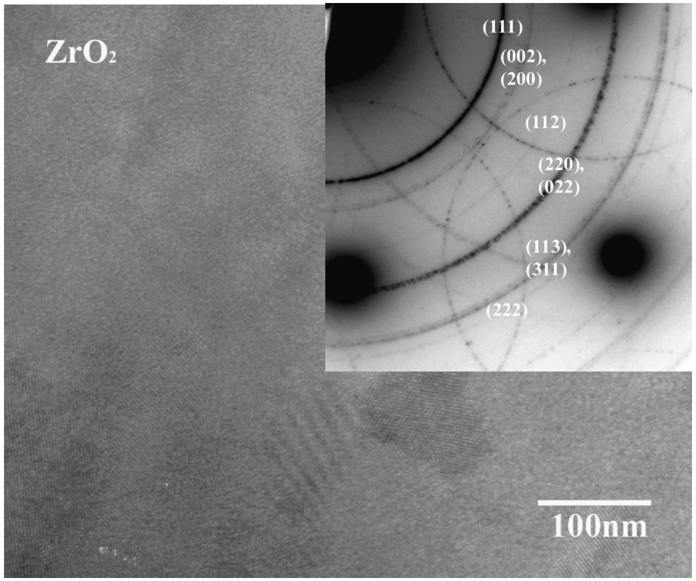
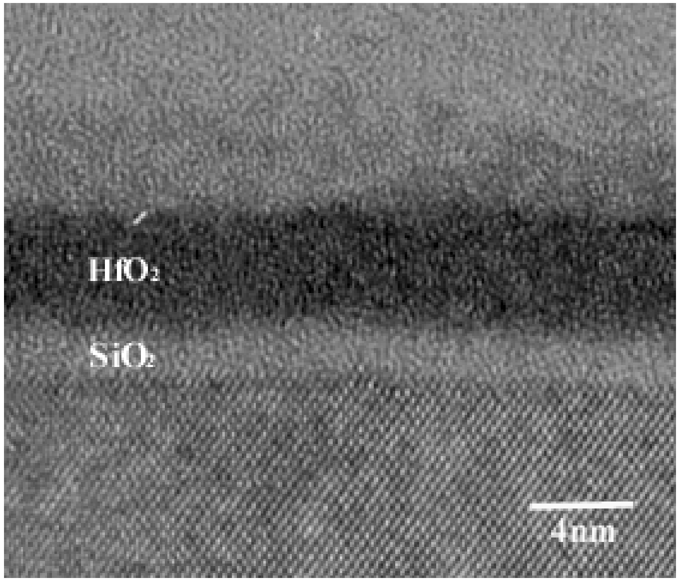
Microstructure of As-grown ALD ZrO_2

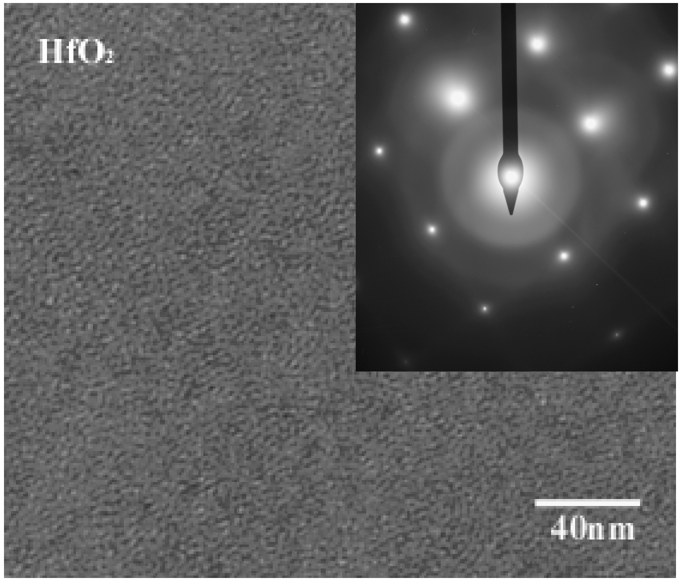




- ZrO_2 film was grown on chemical oxide surface w/o HF strip.
- Film deposited at 250°C contains mainly polycrystalline ZrO_2.
- Indexing of TEM diffraction pattern reveals ***Tetragonal*** ZrO_2
- Interface and surface roughness obtained from TEM and AFM are encouraging.

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 ZrO_2 process condition w/ $ZrCl_4$

Set-up & optimization of HfO_2 process condition w/ $HfCl_4$

Current Status

Experiments (w/Bent group) on Si (100) surface prep. for selective deactivation of ALD

Set-up & optimization of MO_2 process condition w/ metalorganic precursor

Assess chemical utilization & waste generation for both MCl_4 and metalorganic precursor processes