The Effect of Incidental Hafnium and Zirconium Contamination on MOS Processes

Bert Vermeire, Kenneth Delbridge,
Viraj Pandit and Skip Parks

University of Arizona
Tucson, AZ USA

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vermeire@ece.arizona.edu

Purpose

- **PROBLEM**: Trace amounts of Hafnium and Zirconium contamination have an unknown effect on thin oxide yield and reliability.

- **RELEVANT QUESTION**: Under which conditions does Hf or Zr contamination occur? What levels of Hf or Zr contamination are allowable?

- **ANSWER**: Hf or Zr contamination occurs under neutral or caustic conditions, but does not drastically affect GOI.

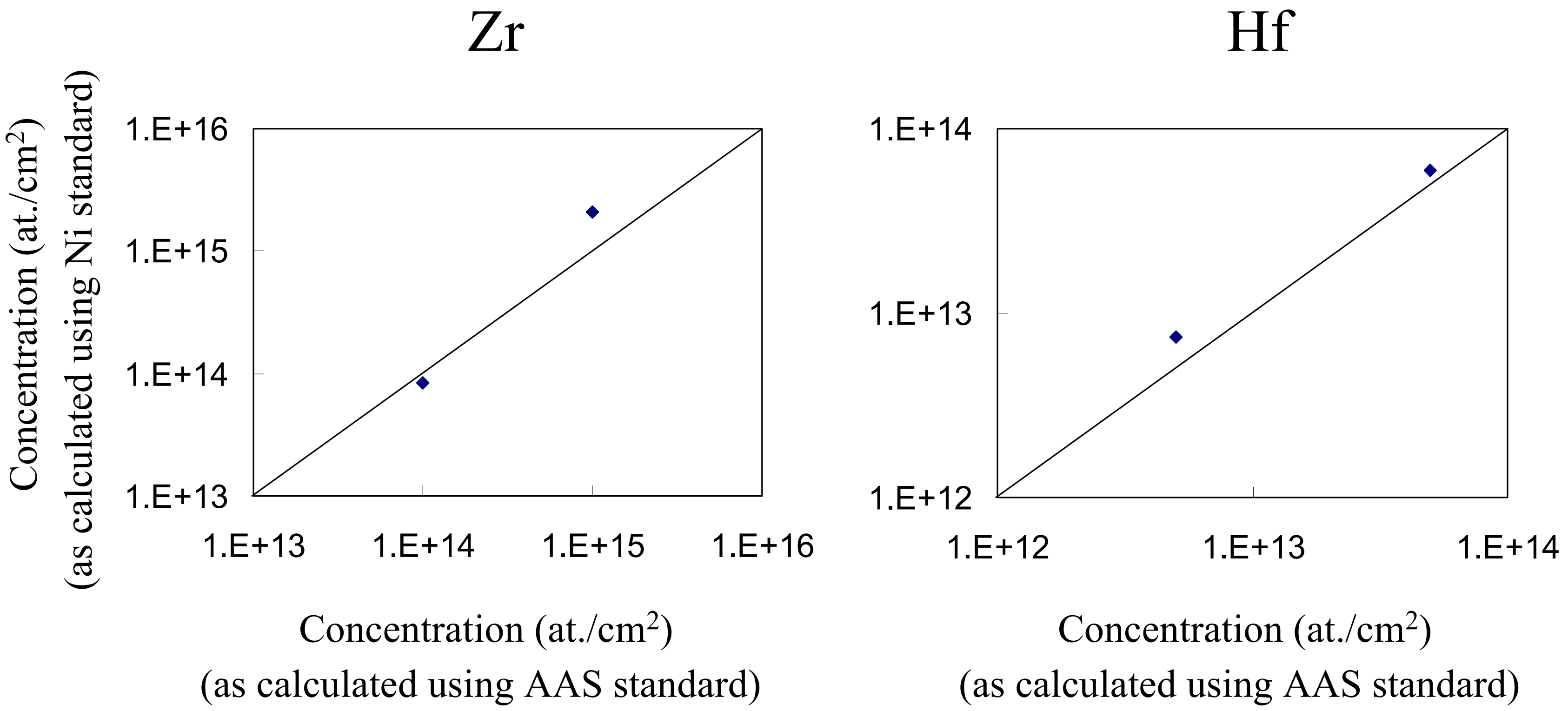
Why Hf & Zr?

- Gate oxide thickness decreases ⇒ Tunnel current increases exponentially
- Need alternate materials with higher dielectric constants to replace SiO_2.
  - $K_{HfO2} = 30$ & $K_{ZrO2} = 25$ vs. $K_{SiO2} = 3.9$
- Thermally stable in direct contact with Si up to high temperatures.
  - Hf forms the most stable oxide
- Pourbaix diagrams for Hf and Zr in aqueous system show that the oxides are stable over a large pH range.

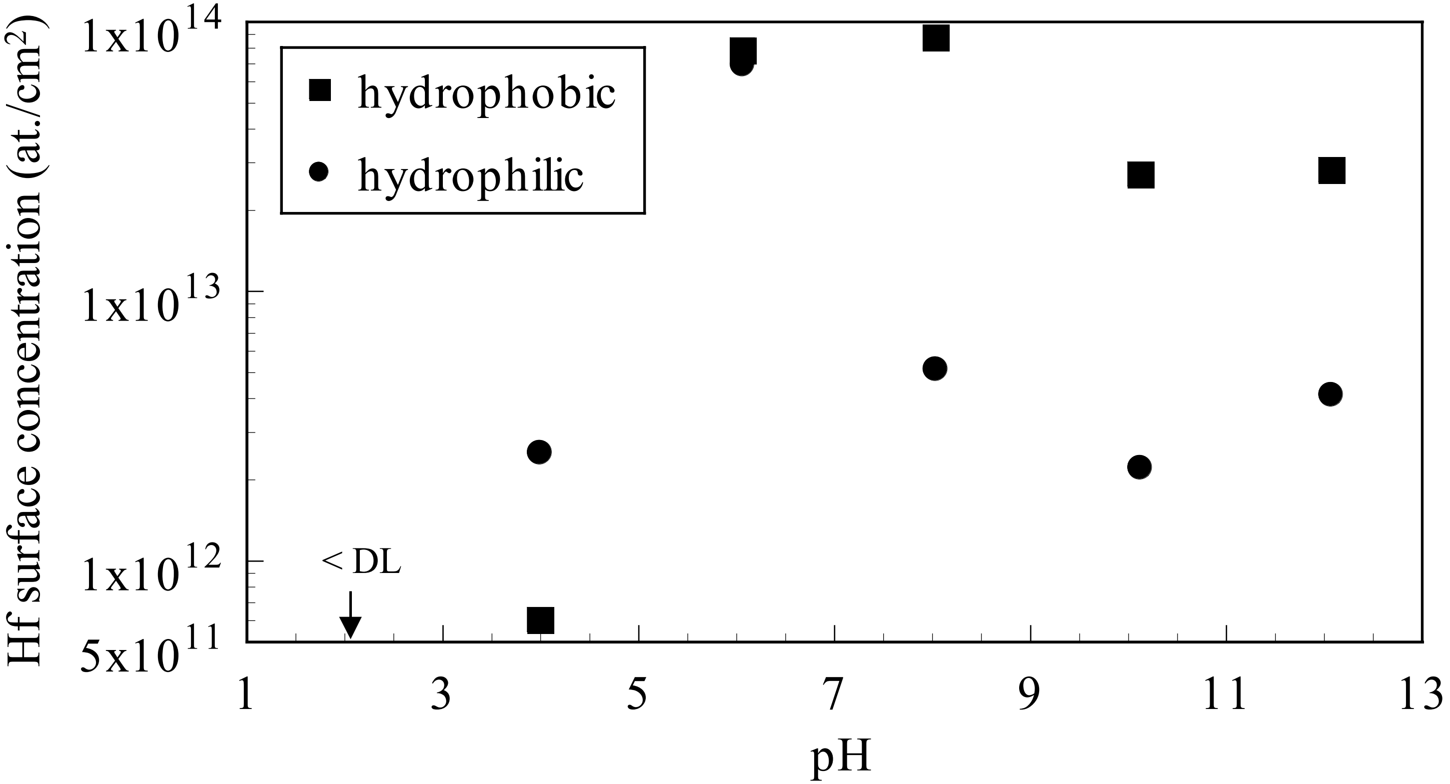
TXRF measurements of Hf and Zr

- Hf is easily distinguished since its Lα peak is not overlapping with a background element.
- The Zr Lα peak is very close to the silicon Kα peak. Its relative sensitivity is also poor. Therefore its detection limit is worse and quantification can be difficult.
- For the first experiments, the TXRF was operating at low intensity (the optical system needed alignment) and at low angle of incidence (software error) and without VPD-DSE. Detection limits have been improved by more than two order of magnitude.

TXRF Standards Verification



Hf adsorption vs. pH

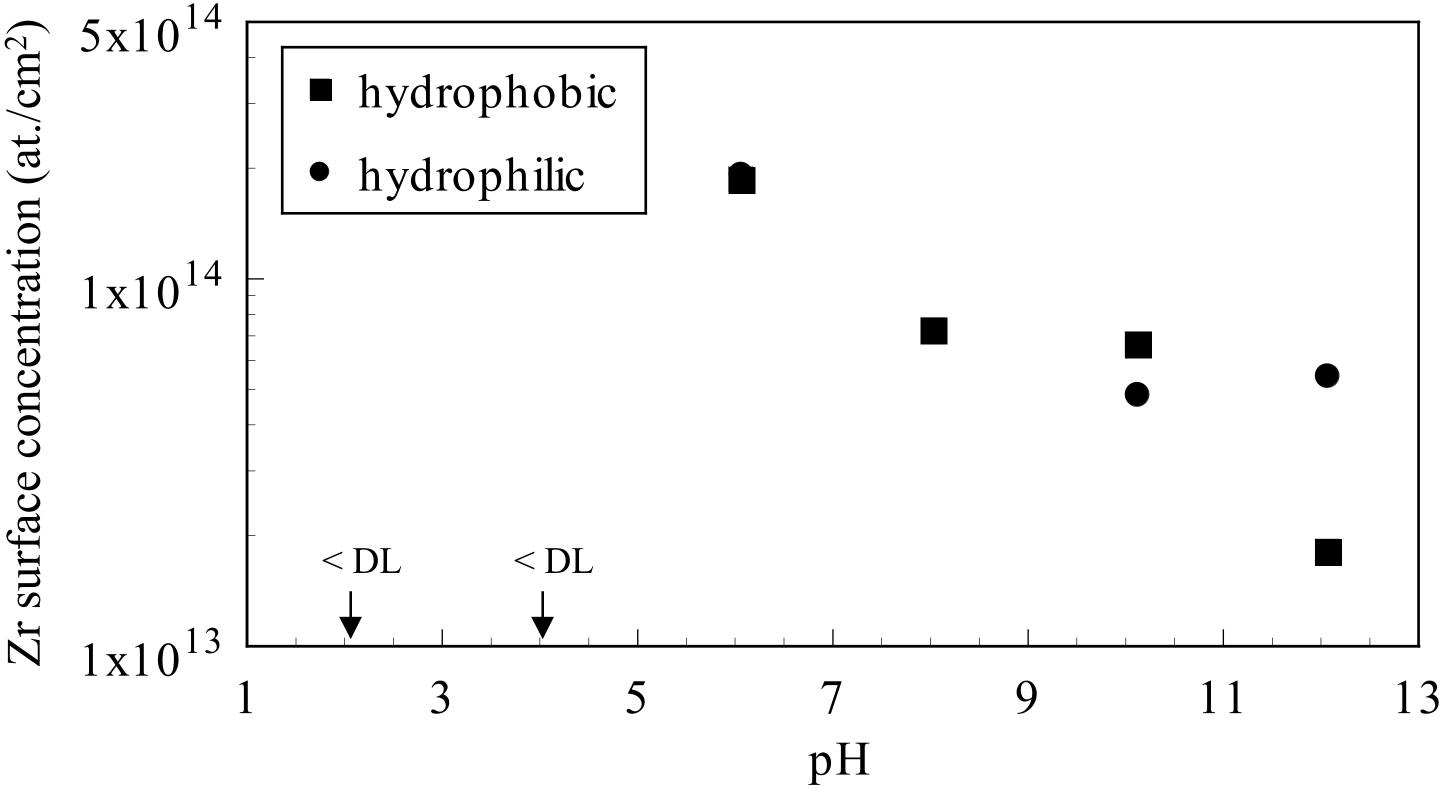


Ionic strength = 0.01 M (NaCl)

Detection Limit = DL = 5×10^{11} at. cm^2

Contamination = 1 ppm

Zr adsorption vs. pH



Ionic strength = 0.01 M (NaCl)

Detection Limit = 1 x 10^{13} at. cm^2

Contamination = 1 ppm

Hf and Zr adsorption

- Hf and Zr do not adsorb onto Si or SiO_2 under strongly acidic conditions.
- Hf and Zr adsorb readily onto Si and SiO_2 under near-neutral and caustic conditions.
- The adsorption is not readily reversible: Hf and Zr are not removed by a 10 min. DI water rinse from wafers that had Hf and Zr deposition in solution of pH 6. This is consistent with a particle contamination mechanism.

Deposition of Hf from APM (SC1) solutions and subsequent removal with a HF or HPM clean

Hf conc.	After APM	After HF	After HPM
100 ppb	1×10^{12}	< D. L.	< D. L.
1000 ppb	8×10^{12}	< D. L.	< D. L.

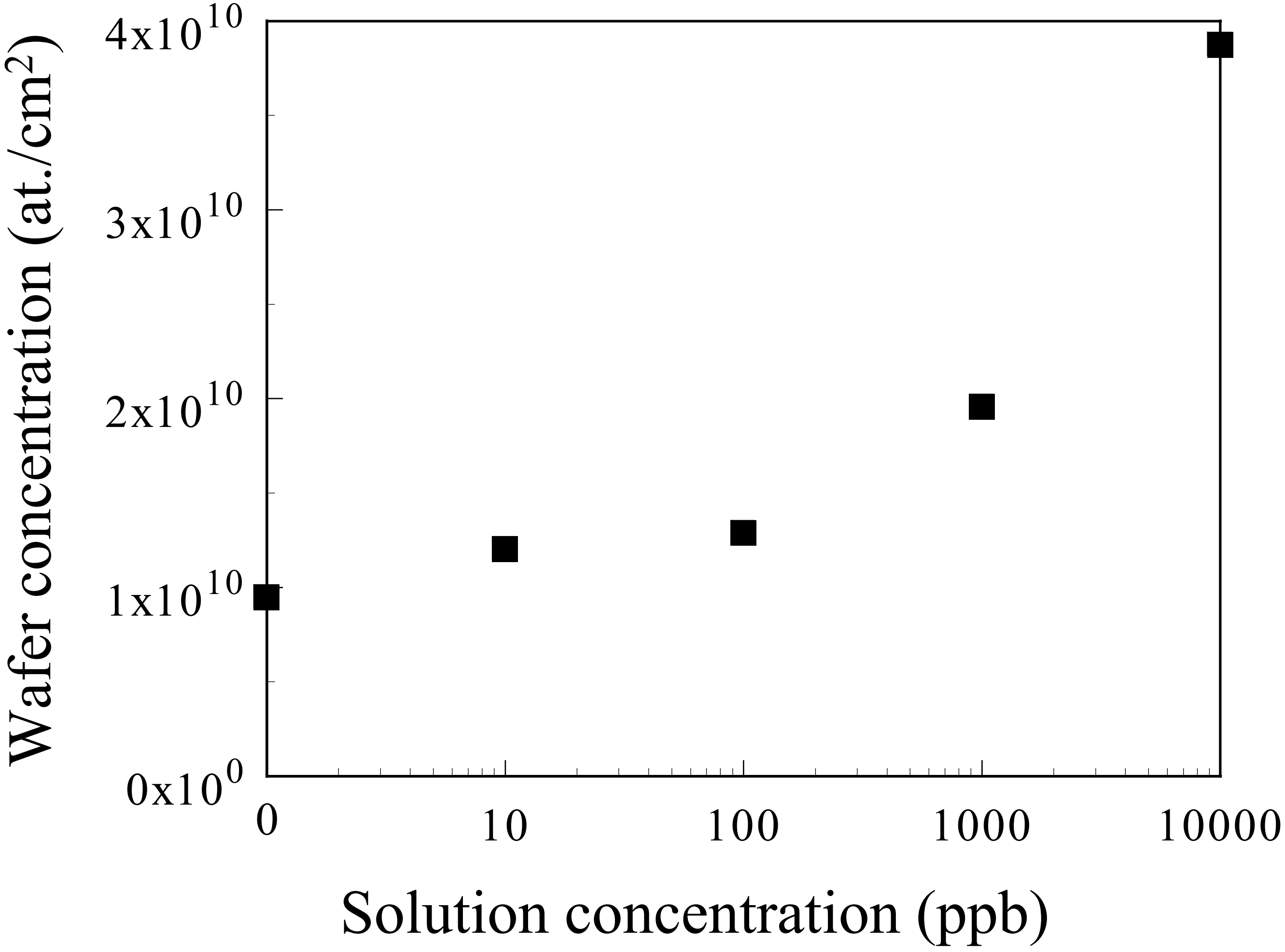
APM:
$NH_4OH : H_2O_2 : H_2O = 1:1:5$
Temp. = 60 °C

HPM:
$HCl : H_2O_2 : H_2O = 1:1:5$
Temp. = 60 °C

HF:
$HF : H_2O = 1:50$
Temp. = room temp.

Hf det. limit = 5×10^{11} at./cm^2

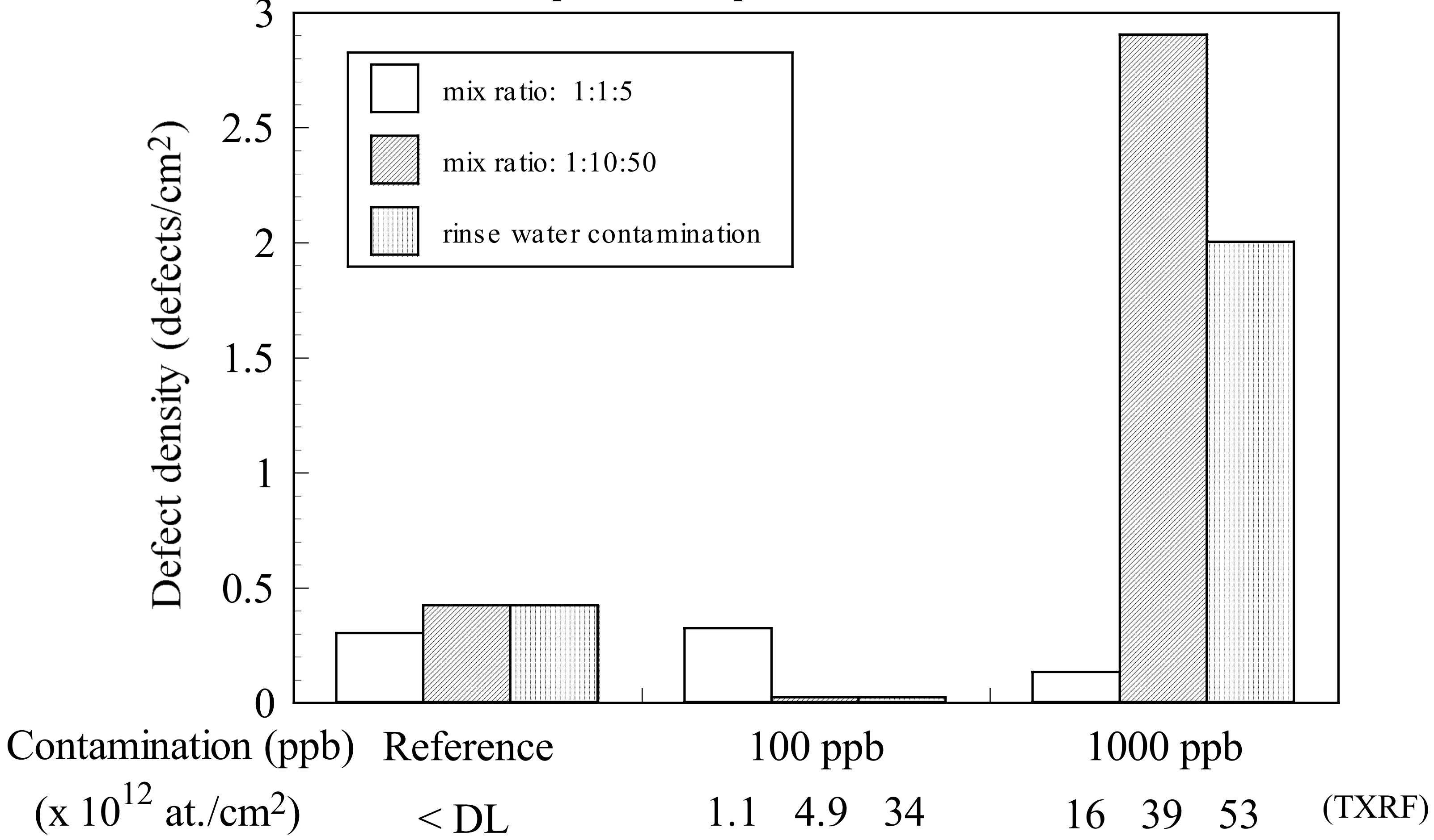
Deposition of Hf from 5% HF



Gate oxide integrity (GOI) testing of Hf or Zr contaminated wafers

- Contamination was introduced using a contaminated APM (SC1) solution or contaminated rinse water.
- Two mix ratio’s of APM were used: 1:1:5 and 1:10:50. Both solutions were at 60 °C. The pH of these solutions was 10.9 and 10.2 respectively.
- A third condition was a final rinse in contaminated rinse water.

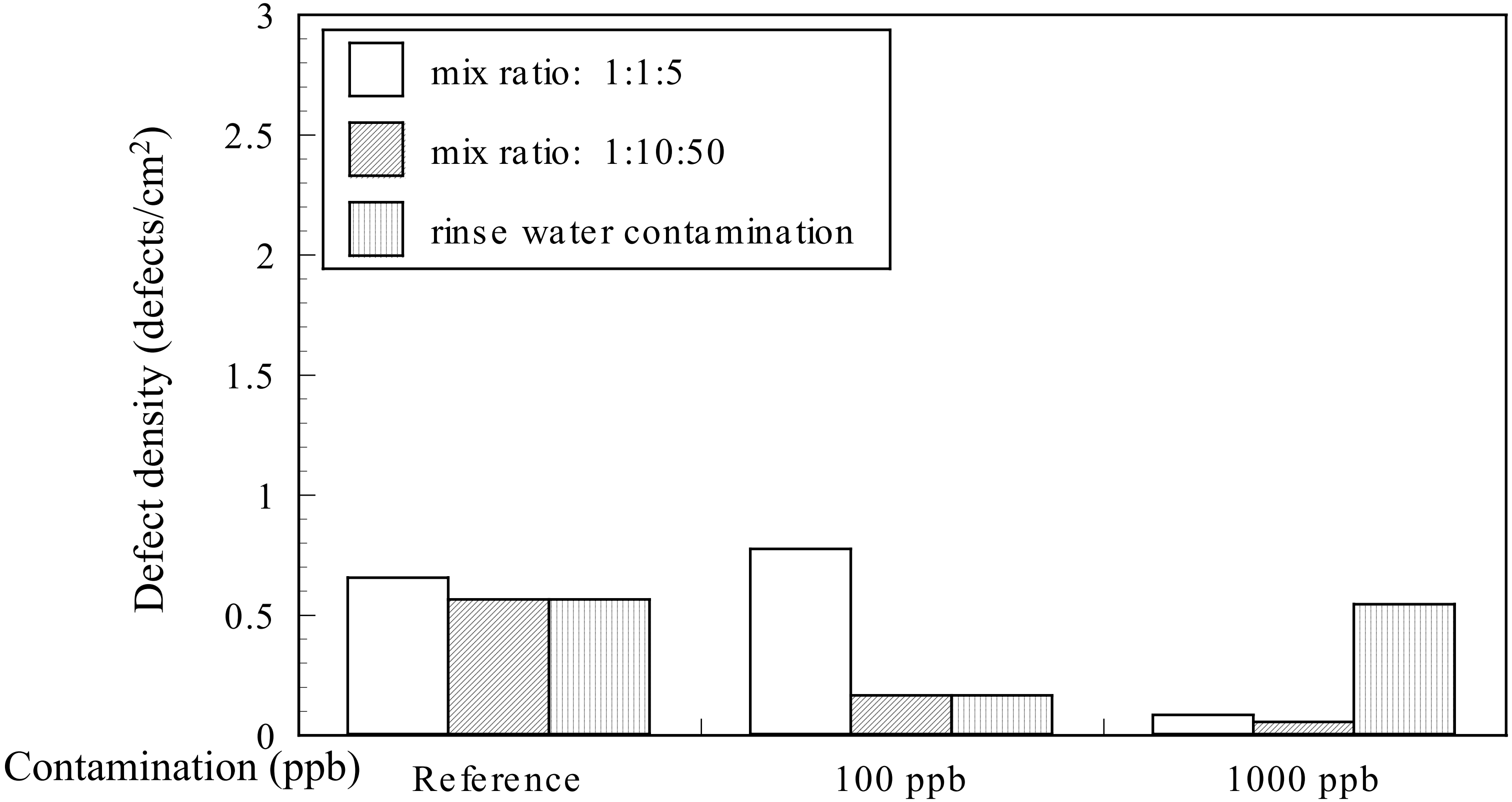
GOI effect for 3 nm oxides with Hf from APM (SC1) or rinse water



Ramped voltage test with
Defect threshold: 12 MV/cm

APM: @ 60 ºC

GOI effect for 3 nm oxides with Zr from APM (SC1) or rinse water



(VPD-DSE-TXRF) < DL 1.1 2.8 46 12 7.5 n/a (10^{12} at./cm^2)

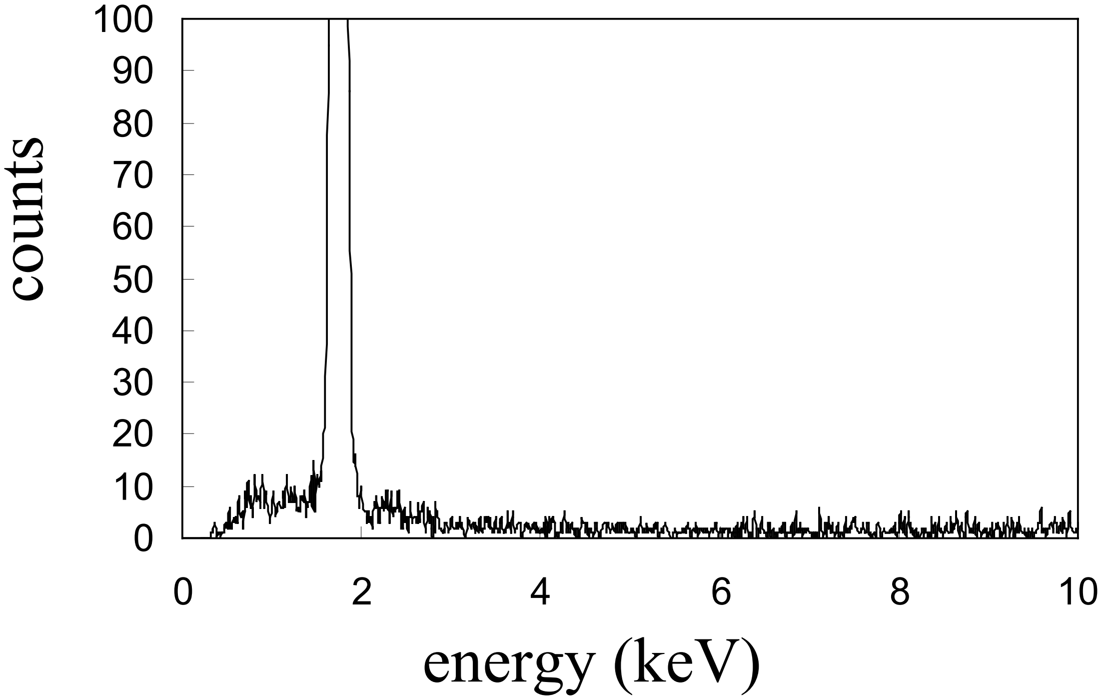
Ramped voltage test with
Defect threshold: 12 MV/cm

APM: @ 60 ºC

Redistribution of Hf and Zr during oxidation

- Residual contamination in the oxide/at the silicon-SiO_2 surface can be measured after vapor phase decomposition (VPD).
- Residual Hf contamination after oxidation is found to account for all the Hf introduced prior to the oxidation (within experimental error).
- From this, it can be concluded that most (if not all) Hf contamination remains in the oxide or at the Si-SiO_2 surface.

TXRF scan of cross contamination monitor wafer



No Hf contamination was observed on a clean wafer inserted between two highly contaminated (> 10^{13} atoms/cm^2) wafers.

Cross contamination during thermal processing

- Clean wafers were placed above and below a wafer with ZrO_2 and annealed at 950 °C for two hours in a nitrogen ambient. Polished side was facing the ZrO_2 wafer.
- Wafers were evaluated by AMD using TXRF (detection limit = 2×10^{11} atoms/cm^2) at five wafer positions.
- Two spots on the bottom wafer contained detectable quantities of Zr.

Conclusions for Hf and Zr contamination

- Hf & Zr contamination from APM (SC1) does not appear to be detrimental to the gate oxide until very high contamination levels are present.
- Near neutral solution conditions offer most potential for problems.
- Slight decomposition of the peroxide (starting at 100 ppb concentration of Hf or Zr) limits the APM bath lifetime.
- Acid cleans (dilute HF and HPM (SC2)) effectively remove contamination. Very little deposition from highly contaminated HF is observed.

Conclusions (continued)

- Contamination introduced by adsorption during a rinse is not removed by a subsequent clean rinse.
- Trace amounts of contamination present on a wafer prior to oxidation will largely remain in the oxide.
- Cross contamination has been observed during thermal treatment but requires further study.