"In-Situ" Monitoring of Metal Contamination in Dilute HF below 100 ppt

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ENVIRONMENTALLY BENIGN
FRONT-END-OF-LINE SURFACE PREP

Cost of Ownership = \frac{(Fixed \ Cost + Operating \ Cost)}{Yield \times Throughput \times Utilization}

- **In-Situ** Bath Contamination Monitoring
  - Maintains yields
  - Increases tool utilization
  - Reduces consumables

- 25% of process steps

Average annual fab consumption
- 5 GWh electricity
- 240 million gallons water
- 300 tons hazardous chemicals

NSF/SRC Engineering Research Center for Environmentally Benign Semiconductor Manufacturing
TRACE METALS AND GOI

- Less pure solutions lead to low-field (Mode I) breakdown
- Thinner oxides more sensitive to contamination

Weibull Distribution

$$F = 1 - \exp(-CE^b)$$
IN-SITU PERFORMANCE MONITORING

- Purifier binds metals with macrocycle ligands
- Remaining reducible metals deposit on silicon wafer
- Metals detected as change in minority carrier lifetime
HIGH SENSITIVITY MEASUREMENT OF SURFACE STATES

- Recombination occurs at surface and bulk sites

\[
\frac{1}{\tau_{\text{meas}}} = \frac{1}{\tau_{\text{bulk}}} + \frac{1}{\tau_{\text{surf}}}
\]

\[
\tau_{\text{meas}} \approx \frac{d^2}{D \pi^2}
\]

\[
\tau_{\text{meas}} \approx \frac{d}{2S}
\]

\[
\tau_{\text{bulk}} = 10\text{ms}
\]

Limited by:
- Diffusion
- Surface Recombination
- Bulk Recombination
METAL DEPOSITION FROM FLOWING SOLUTIONS

- Surface reaction
  \[
  \frac{d[Cu]_{surf}}{dt} = -k \times [Cu]^* 
  \]

- Diffusion across boundary layer
  \[
  J_{Cu} = \frac{D_{Cu} \times ([Cu]_{bath} - [Cu]^*)}{\delta} 
  \]

- Static boundary layer present in laminar flow
METAL DEPOSITION FROM FLOWING SOLUTIONS

- Transient behavior
  - deposition of near-surface metals
  - surface roughening

- Steady-state deposition

\[
\frac{d[Cu]_{surf}}{dt} = [Cu]_{bath} \left( \frac{1}{k + \delta/D} \right)
\]
IN-SITU DETECTION OF CU DEPOSITION FROM DILUTE HF

- Change in lifetime indicates metal deposition

**Cu Coverage (10^{11}/cm^2)**

**Time (s)**

0  4000  8000  12000

1 ppb Cu

2 ppb Cu

3 ppb Cu

$\propto t$
IMPACT OF HF DILUTION ON DEPOSITION RATE

• Dilution enhances deposition rate by 15x
PROPOSED MODEL

• Two competing cathodic reactions:

\[ 2H^+ + 2e^- \rightarrow H_2 \]

\[ Cu^{++} + 2e^- \rightarrow Cu \]

• Dilution of HF limits \( H_2 \) formation
CONCLUSION

• Gate Oxide Integrity degraded by sub-ppb metal contamination

• In-situ contamination monitor capable of quantitative analysis below 20 ppt Cu

• Dilution of HF from .5 wt% to .1 wt% increases measured deposition rate by 15x