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

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ENVIRONMENTALLY BENIGN FRONT-END-OF-LINE SURFACE PREP

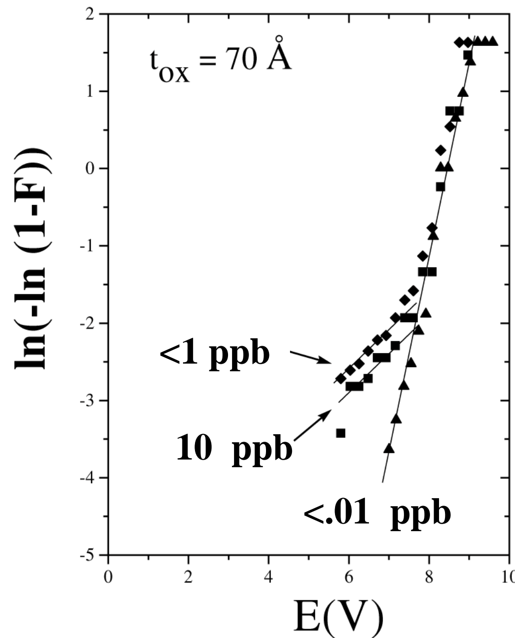
$$Cost\ of\ Ownership = \frac{(Fixed\ Cost + Operating\ Cost)}{Yield \times Throughput \times Utilization}$$

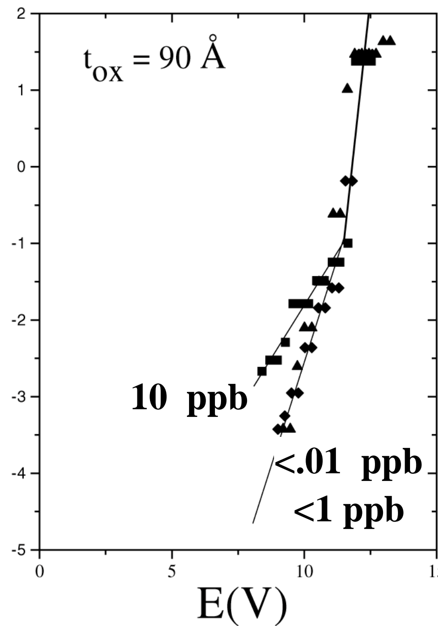
- ***In-Situ* Bath Contamination Monitoring**
  - **Maintains yields**
  - **Increases tool utilization**
  - **Reduces consumables**

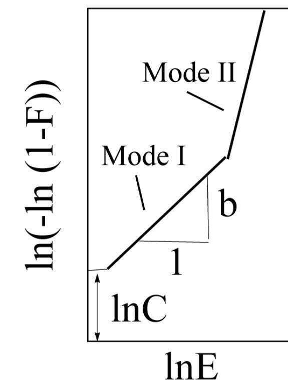
25% of process steps

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

TRACE METALS AND GOI





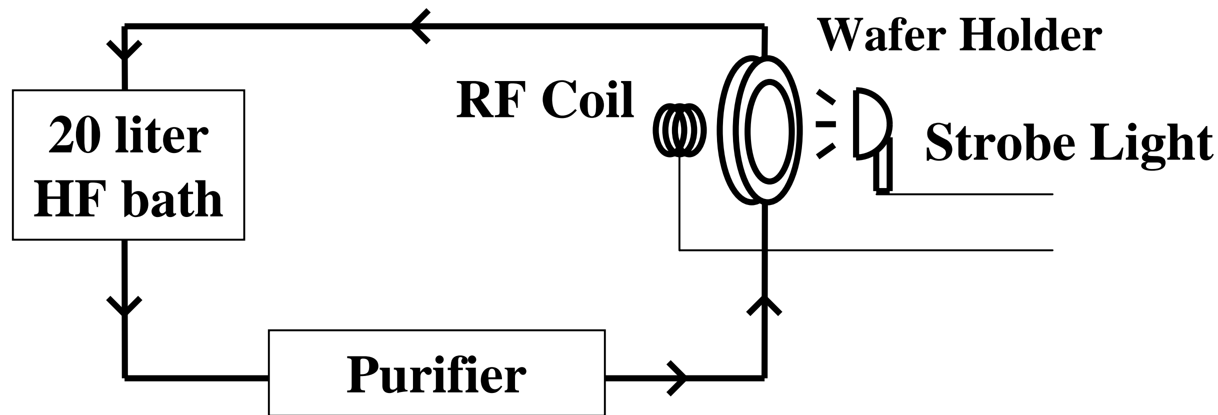


Weibull Distribution

$$F = 1 - \exp(-CE^{b})$$

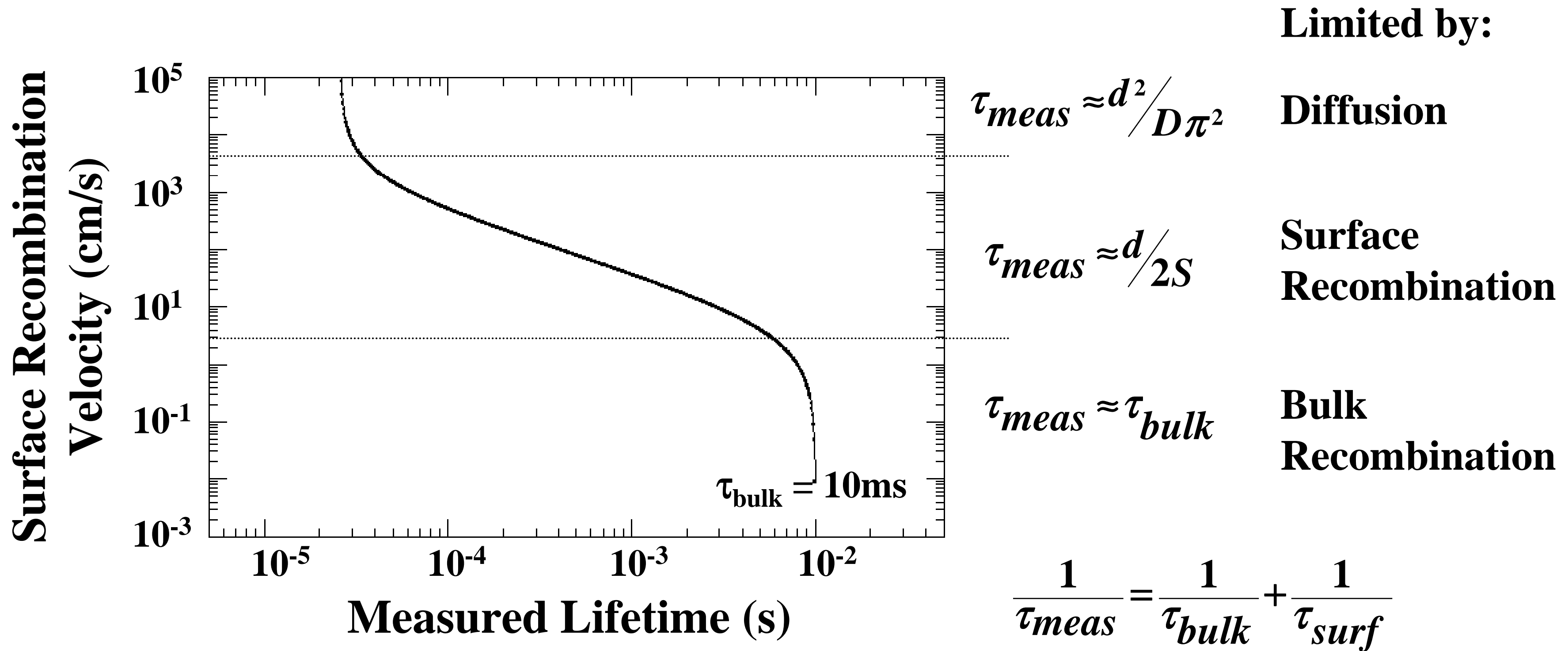
- **Less pure solutions lead to low-field (Mode I) breakdown**
- **Thinner oxides more sensitive to contamination**

IN-SITU PERFORMANCE MONTORING



- Purifier binds metals with macrocycle ligands
- Remaining reducible metals deposit on silicon wafer
- Metals detected as change in minority carrier lifetime

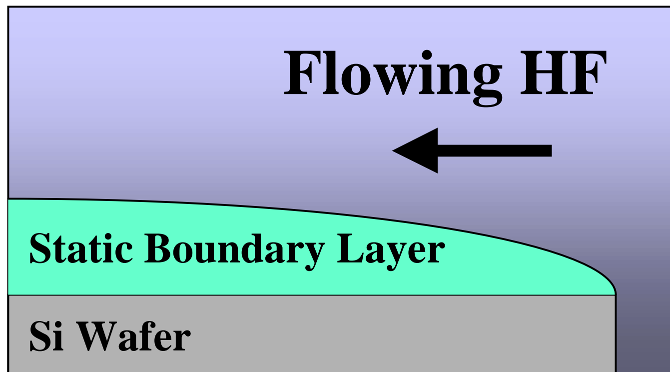
HIGH SENSITIVITY MEASUREMENT OF SURFACE STATES



$$\frac{1}{\tau_{meas}} = \frac{1}{\tau_{bulk}} + \frac{1}{\tau_{surf}}$$

- **Recombination occurs at surface and bulk sites**

METAL DEPOSITION FROM FLOWING SOLUTIONS



- Surface reaction

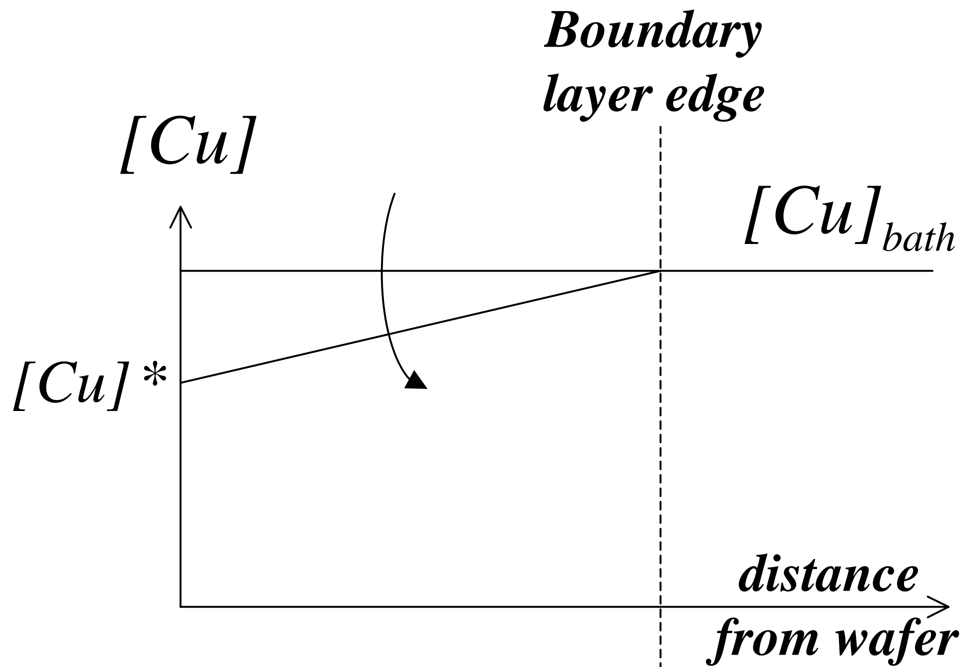
$$\frac{d[Cu]_{surf}}{dt} = -k \times [Cu]^*$$

- Diffusion across boundary layer

$$J_{Cu} = \frac{D_{Cu} \times ([Cu]_{bath} - [Cu]^*)}{\delta}$$

- Static boundary layer present in laminar flow

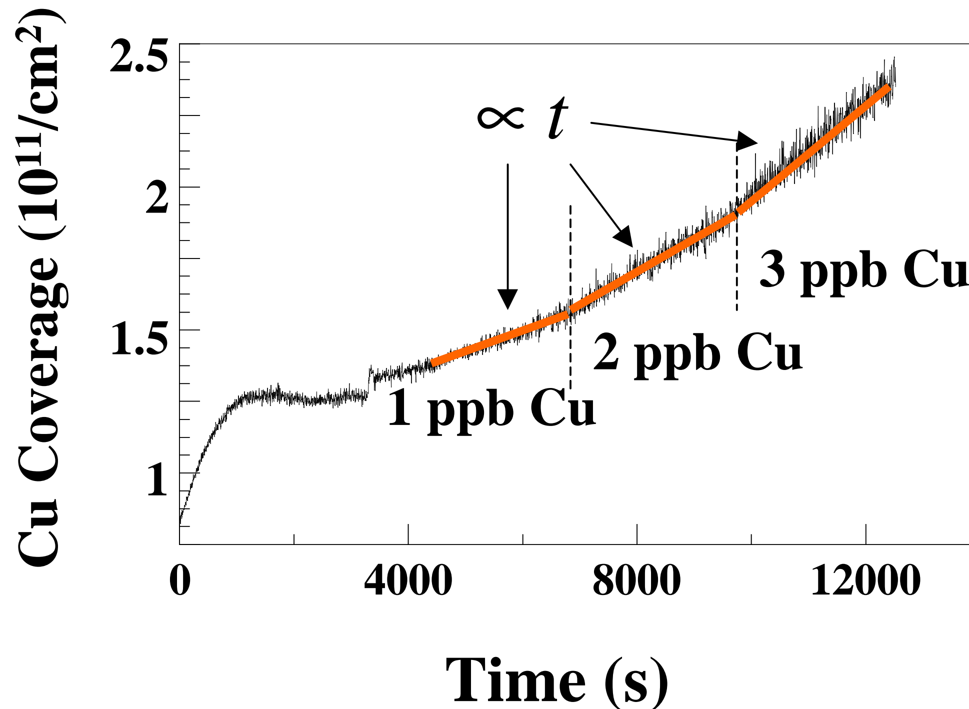
METAL DEPOSITION FROM FLOWING SOLUTIONS



- **Transient behavior**
  - **deposition of near-surface metals**
  - **surface roughening**
- **Steady-state deposition**

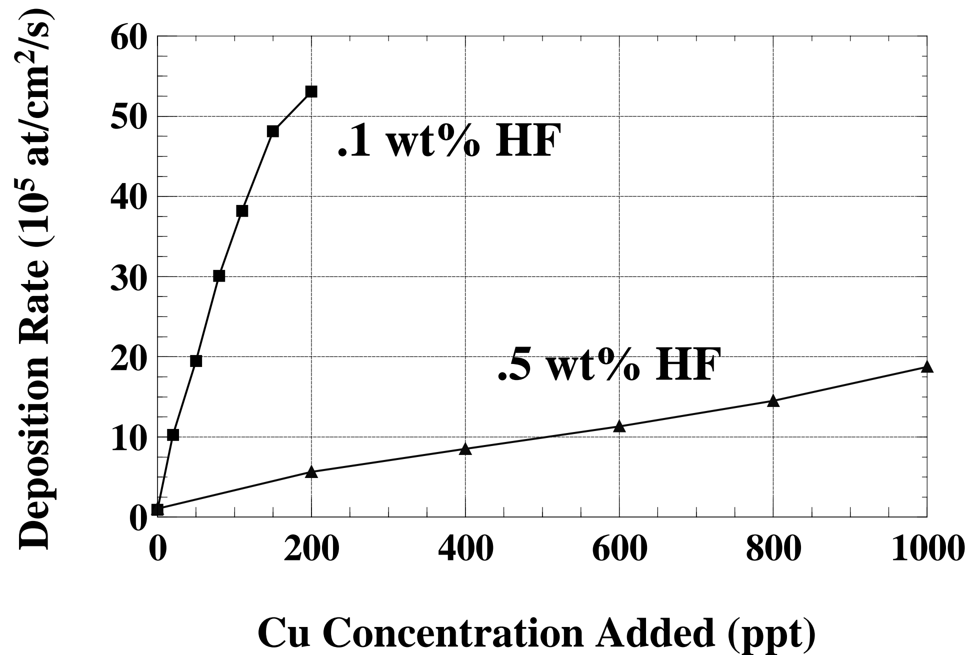
$$\frac{d[Cu]_{surf}}{dt} = [Cu]_{bath}\left(\frac{1}{1/k + \delta/D}\right)$$

IN-SITU DETECTION OF CU DEPOSITION FROM DILUTE HF



- **Change in lifetime indicates metal deposition**

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**