In-Situ Monitoring of ppt-level Metallic Contamination For Point-of-Use HF Reprocessing

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COST OF OWNERSHIP AND WAFER CLEANING

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

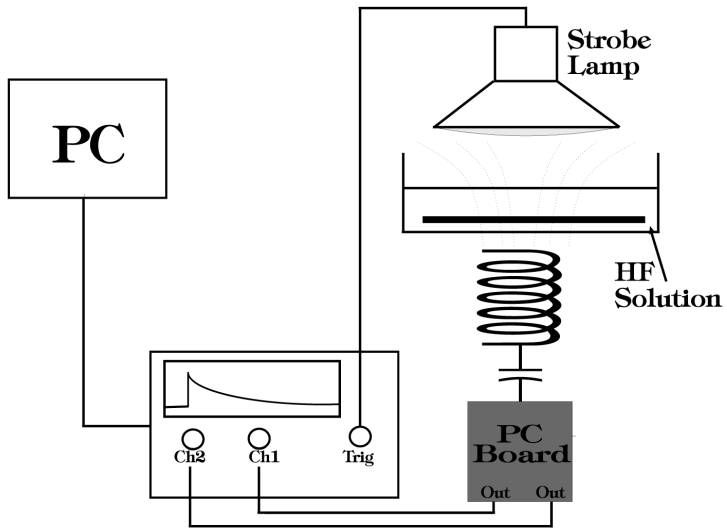
- Yield and Throughput
  - Design and prototyping of *in-situ* metal contamination monitor

25% of process steps

- Materials Cost and Utilization
  - Modeling of HF dilution and metal deposition

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

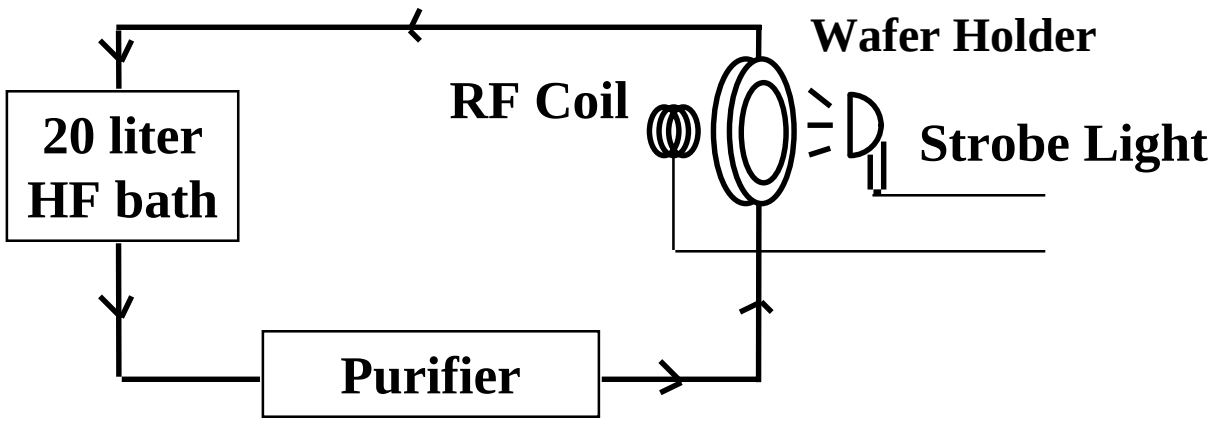
MINORITY CARRIER LIFETIME MEASUREMENT BY RF-PCD



- **Strobe lamp injects excess carriers**
- **RF coil monitors wafer conductivity**
- **Density of recombination centers determines decay rate**

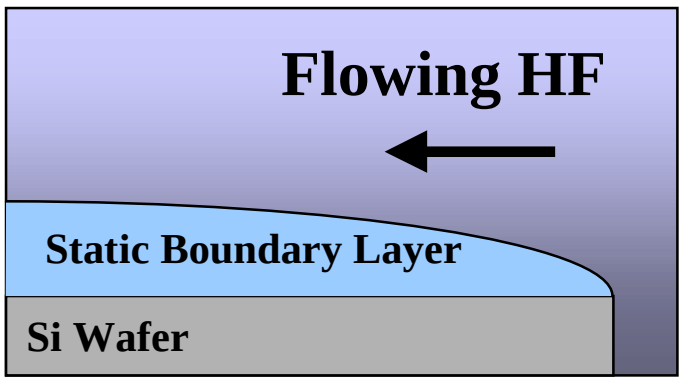
- **RF-PCD allows for fast, in-situ lifetime measurements**

HF RECYCLING SYSTEM



- **Cost of Ownership**
  - **Bath life extension**
  - **Yield excursions**
- **Environmental Impact**
  - **Chemical consumption**
  - **Dilution**

METAL DEPOSITION FROM FLOWING SOLUTIONS



- **Surface reaction**

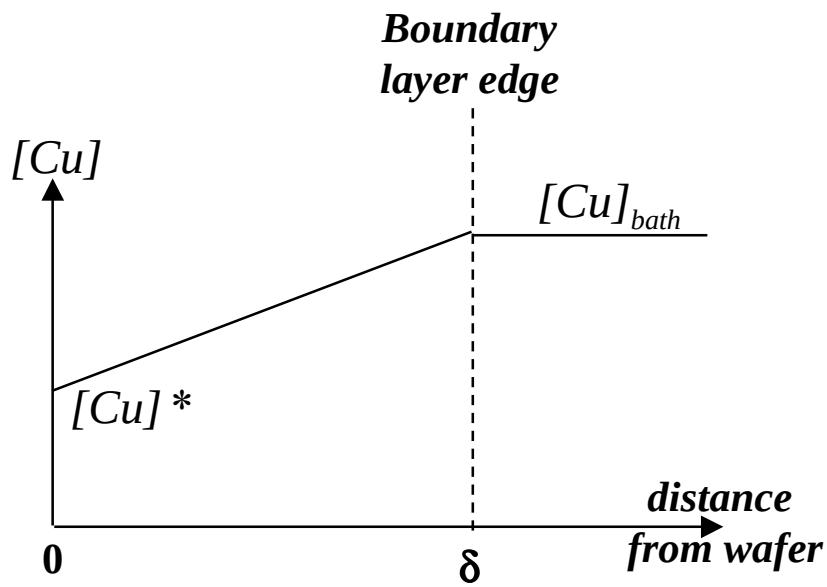
$$\frac{d[Cu]_{surf}}{dt} = -k \times [Cu]^*$$

- **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

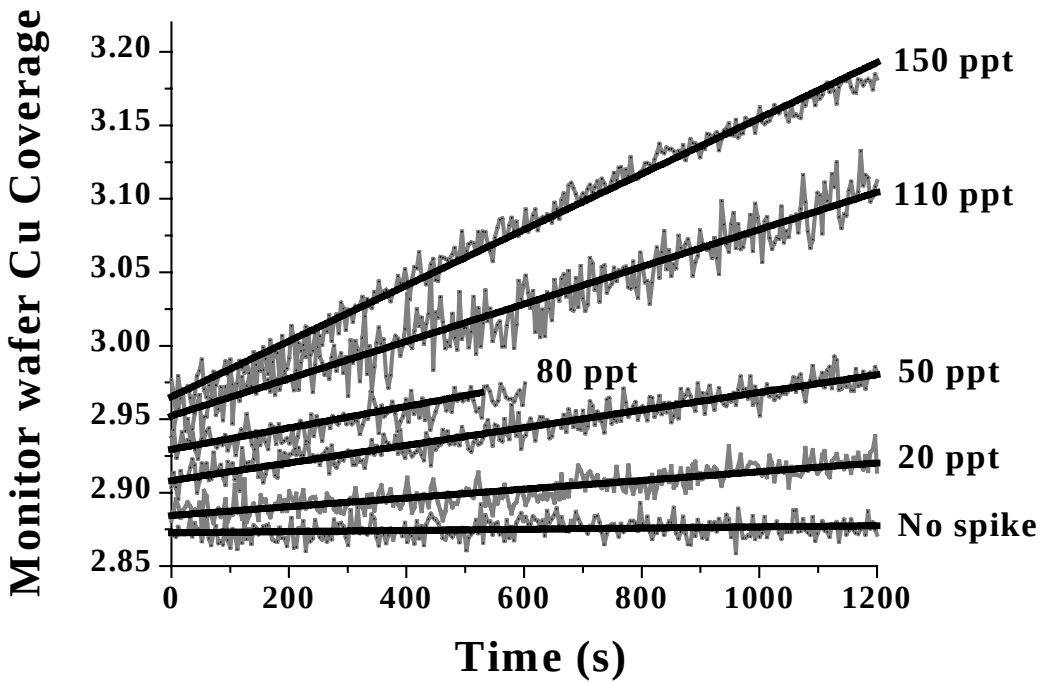


- **Transient behavior**
  - **deposition of near-surface metals**
  - **surface roughening**
- **Steady-state deposition**

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

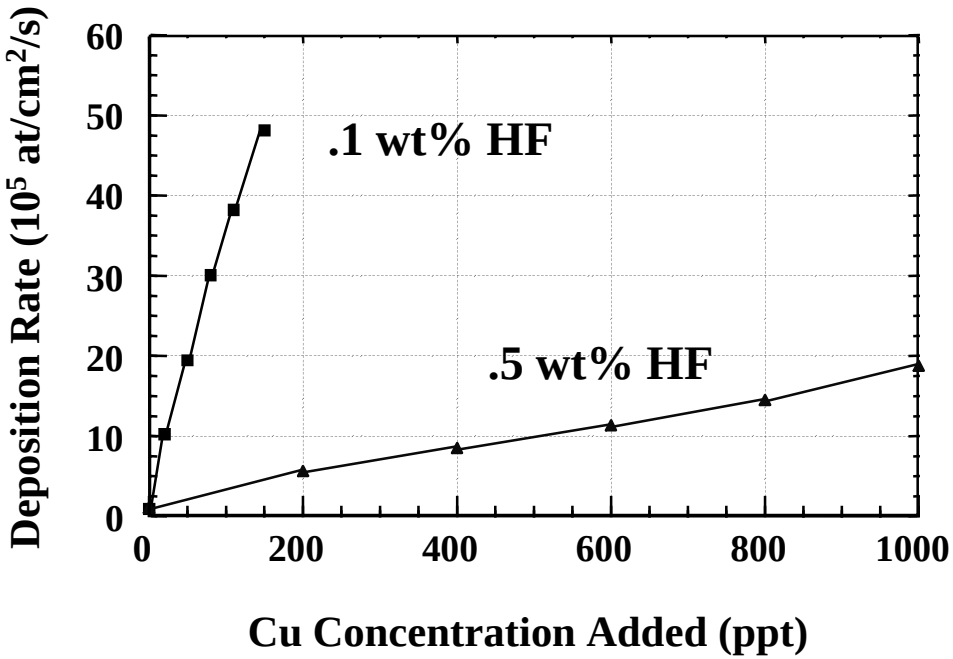
- **Diffusion flux constant under steady-state conditions**

METAL DETECTION: *IN-SITU* MEASUREMENT



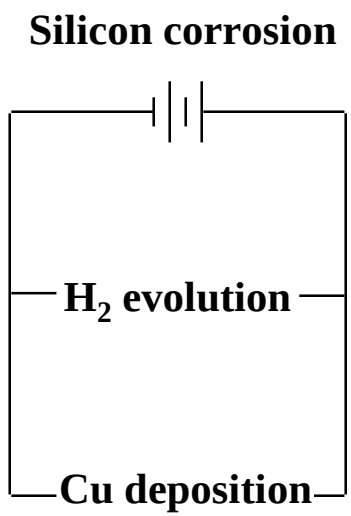
- **Monitor sensitive to ppt metal contamination**

IMPACT OF HF DILUTION ON DEPOSITION RATE



- **Dilution enhances deposition rate by 15x**

Si ELECTROCHEMISTRY



Anodic Half Reaction:

$$Si + 6F^- \rightarrow SiF_6^{-2} + 4e^-$$

Cathodic Half Reactions:

$$2H^+ + 2e^- \rightarrow H_2$$

$$Cu^{++} + 2e^- \rightarrow Cu$$

- **Cu reduction competes with H_2 evolution**

ELECTROCHEMICAL REACTION RATES

Reaction slow step:

Reaction rate:

$Si + F^- \rightarrow Si\text{-}F + e^-$

$$j_{Si} = k_{Si}[F^-]e^{n_{si}(1-\alpha_{si})(E-E_1)/\phi}$$

$2H^+ + 2e^- \rightarrow H_2$

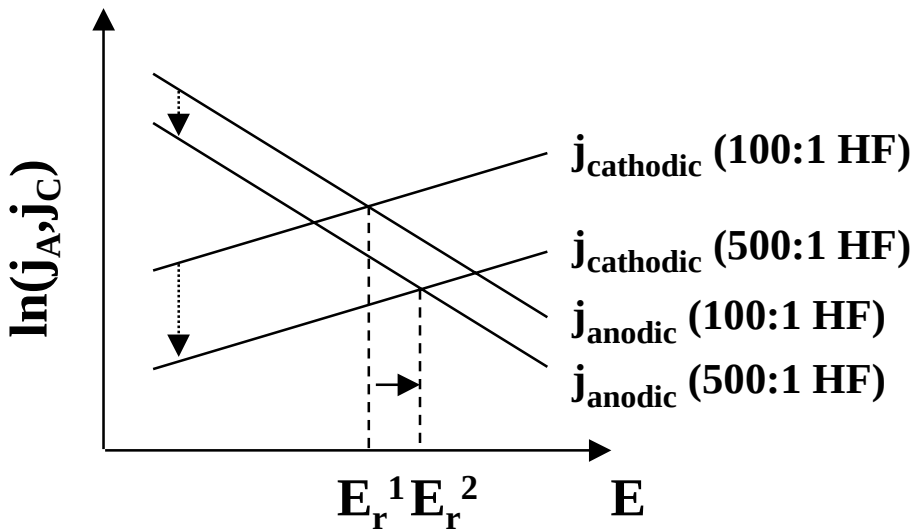
$$j_H = k_H[H^+]^2 e^{-n_H\alpha_H(E-E_2)/\phi}$$

$Cu^{++} + 2e^- \rightarrow Cu$

$$j_{Cu} = k_{Cu}[Cu^{2+}]e^{-n_{Cu}\alpha_{Cu}(E-E_3)/\phi}$$

- **Slow step determines reaction kinetics**

DEPENDENCE OF POTENTIAL ON HF DILUTION



- For low contamination levels, H_2 evolution dominates $j_{cathodic}$
- Shift to more cathodic potential increases Cu deposition rate

- Potential at surface shifts with dilution

Cu DEPOSITION RATE

- ***E*** **determined by** $j_{Si} \approx j_H$**:**

$$j_{Cu} \propto [H^+]^{-n_{Cu}\alpha_{Cu}/(n_{Si}(1-\alpha_{Si})+n_H\alpha_H)}$$

- **We measure an exponent of 1.78**
- **Bertagna *et al.*(JECS, 144, p. 4715) measure** $n_{Si}(1-\alpha_{Si})=0.12$ **and** $n_H\alpha_H=0.35$

→ $\alpha_{Cu}=0.42$

- **For a D:1 bath of (DI Water) : (49% HF)**

$$\text{Cu Deposition Rate} \propto [Cu^{+2}]D^{1.78}$$

- **Bath purity requirement scales with** $D^{1.78}$

CONCLUSIONS

- **We demonstrate *in-situ* detection of 20 ppt Cu in 500:1 HF.**
- **Measured deposition rate from 500:1 HF is 17.5 times faster than from 100:1 HF.**
- **We quantify the potential shift at surface and relate deposition rate to bath dilution.**