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Atmospheric Degradation of Connector Materials

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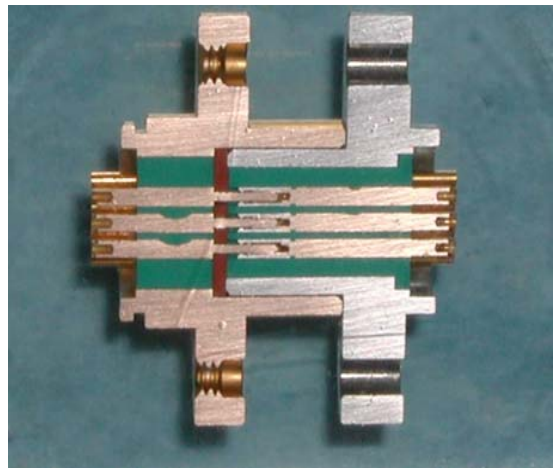
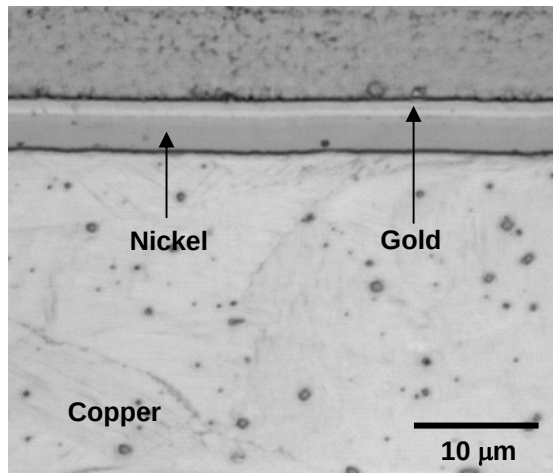
Current level of understanding is insufficient to predict long term component performance

- Atmospheric corrosion of gold plated copper features used in electrical and electronic devices can impact their reliability and effective service life.
- Critical need for a model which can predict long term performance based upon readily quantifiable environmental parameters
- Effective modeling requires that the relevant corrosion degradation phenomena be understood and the key kinetic parameters determined





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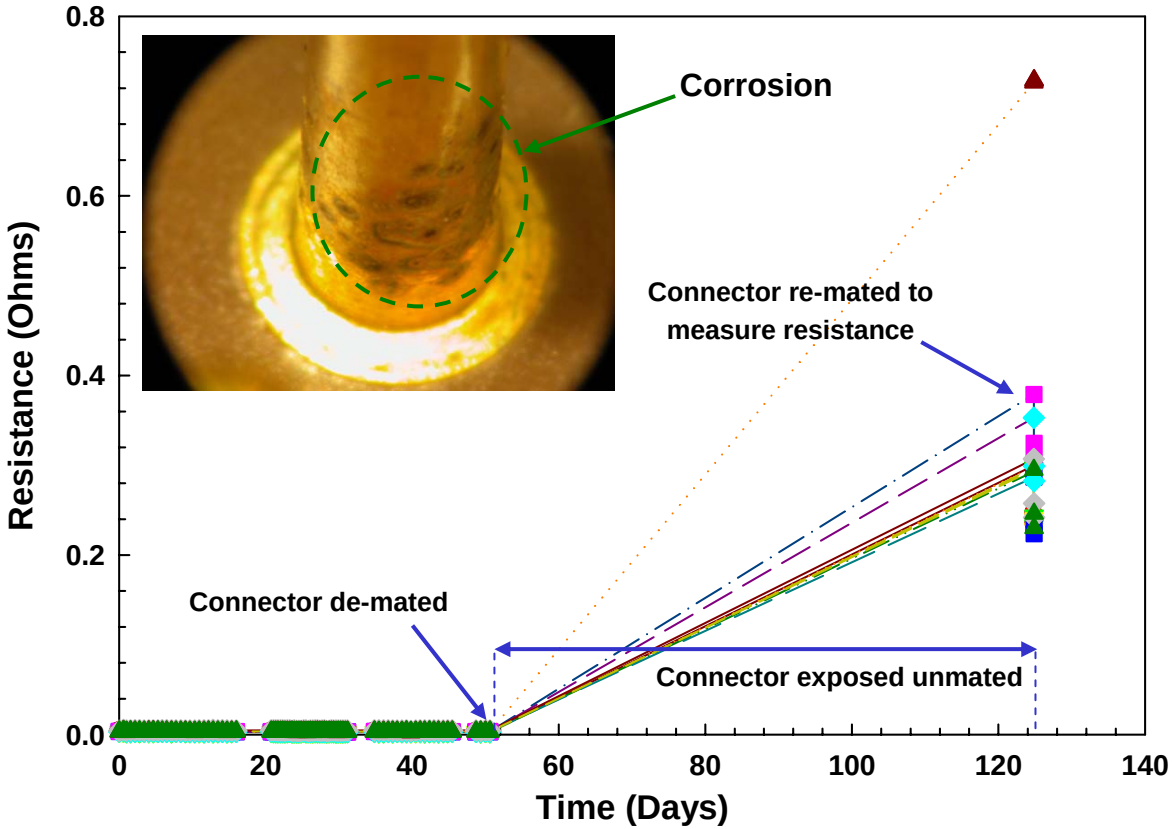
Electrical Behavior of an Aging Connector



courtesy of
Rob Sorensen, SNL

A gold plated connector exposed to a Battelle class II environment.

- Connector functioned properly in the aggressive environment while mated
- While unmated, significant sulfidation occurred
- Remating the connectors revealed a significant increase in the electrical resistance of the connection.

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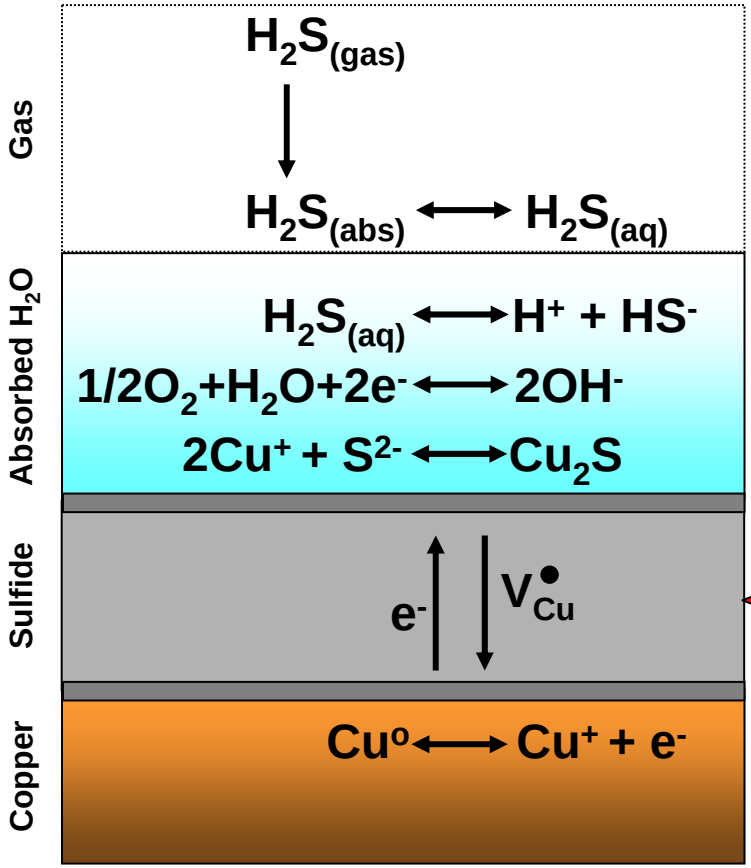
Copper Sulfidation Kinetics



Sulfide / Atmosphere Interface: Surface Reaction

$$J = k_1 C_{H_2S} \exp(-\frac{E_{k1}}{RT}) - k_{-1} C_{v-} C_{h+} \exp(-\frac{E_{k-1}}{RT})$$

Sulfide Layer: Vacancy and Hole Transport

$$2J = D_{0h} \exp(-\frac{E_{Dh}}{RT}) \frac{dC_{h+}}{dy}$$

$$2J = D_{0v} \exp(-\frac{E_{DV}}{RT}) \frac{dC_{V-}}{dy}$$

Copper / Sulfide Interface: Surface Reaction

$$2J = k_2 C_{v-} C_{h+} \exp(-\frac{E_{k2}}{RT})$$

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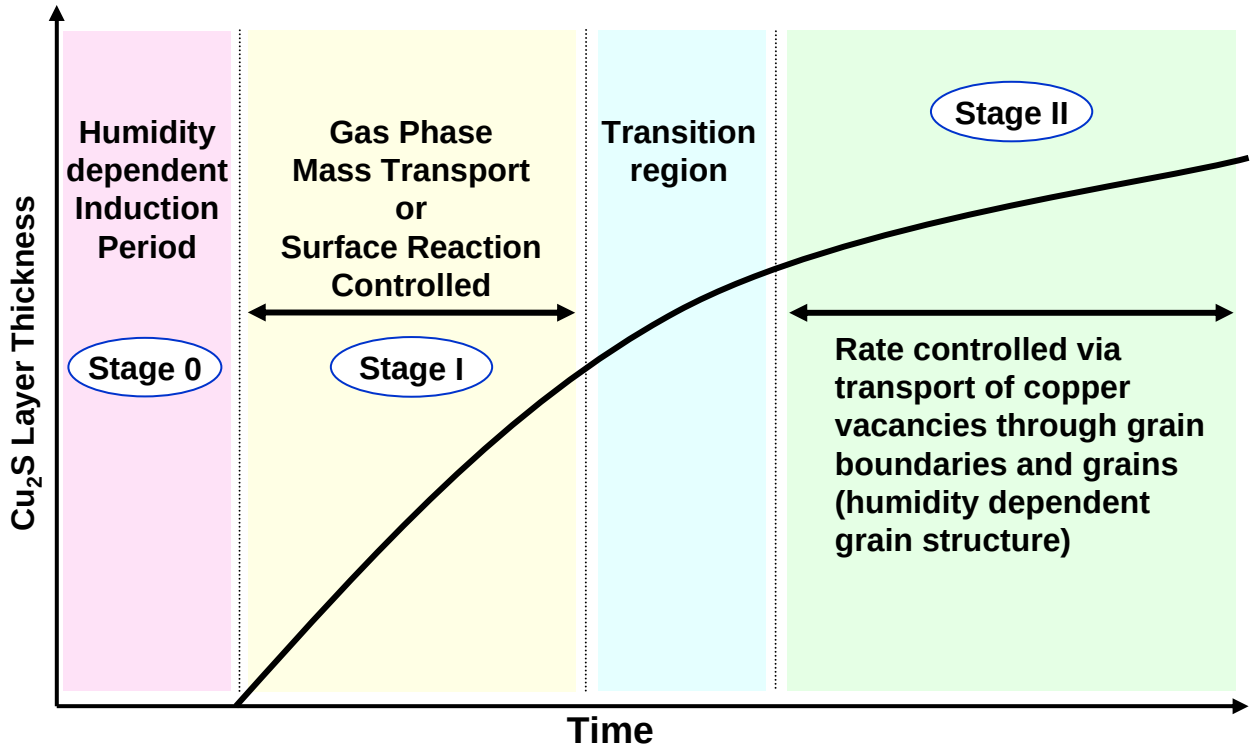
Copper Sulfidation Kinetics



- In *Stage-I*, the sulfidation rate is controlled by either a surface reaction or gas-phase mass transport
- In *Stage-II,* the sulfidation rate is controlled by the diffusion of copper vacancies through the thickening sulfide layer
- Copper sulfide growth occurs unequivocally at the water-gas-sulfide interface.

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The Mathematical Model Consists of Three Sub-Models

Bloom growth sub-model

- Kinetics* – k_1, k_{-1}, k_2
- Diffusivity* – D_v
- *Au* thickness - h_{Au}
- Areal pore density * – M_{pore}
- Initiation *- λ
- Kirkendall voiding * β.
- Pore size distribution *

$$r_{pore}^{L} < r_{pore} < r_{pore}^{U}$$

Time dependent probability distribution of blooms, N(t, A, L)

Morphology sub-model

- Bloom Cutoff factor* - f
- Halo treatment* -
- Wipe (assume none for now)
- Visible Bloom Threshold - r_{VisB}

Thickness of corrosion product Distribution of large blooms.

Contact resistance sub-model

- Multi-level constrictions - A_r/A_n
- Microhardness – H
- Elasticity – E
- Loading force – F
- Surface roughness – σ
- Probe radius – r_{probe}
- Asperity height & numbers* – h_0
- Fraction of metal contacts in asperities * - X_i
- Corrosion product resistivity * - ρ

Cumulative probability distribution of contact resistance as a function of time and environmental conditions CPD(t)

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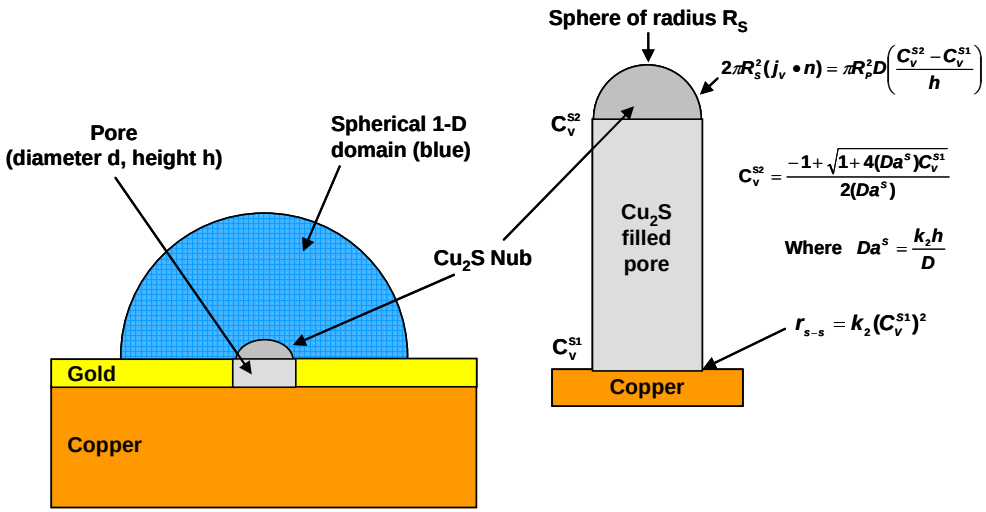
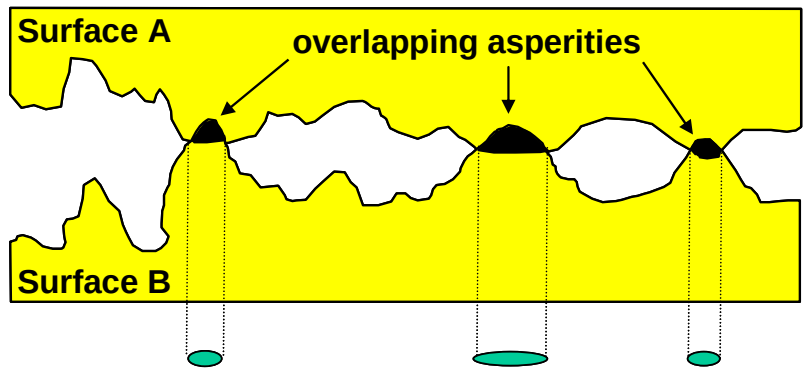
Modeling the contact surface requires that small scale features be accurately captured

- Modeling the sulfidation process and it's impact on the overall performance of a gold plated copper connector requires that a number of key phenomena be captured, namely:
  - Number density and size distribution of corrosion sites as a function of time
  - Mechanical and electrical properties of the resulting corrosion product
  - Nature of the electrical contact (contact area, surface roughness, contact force, etc.)

ASC Model (*9114 - H. Moffat, A. Sun*)





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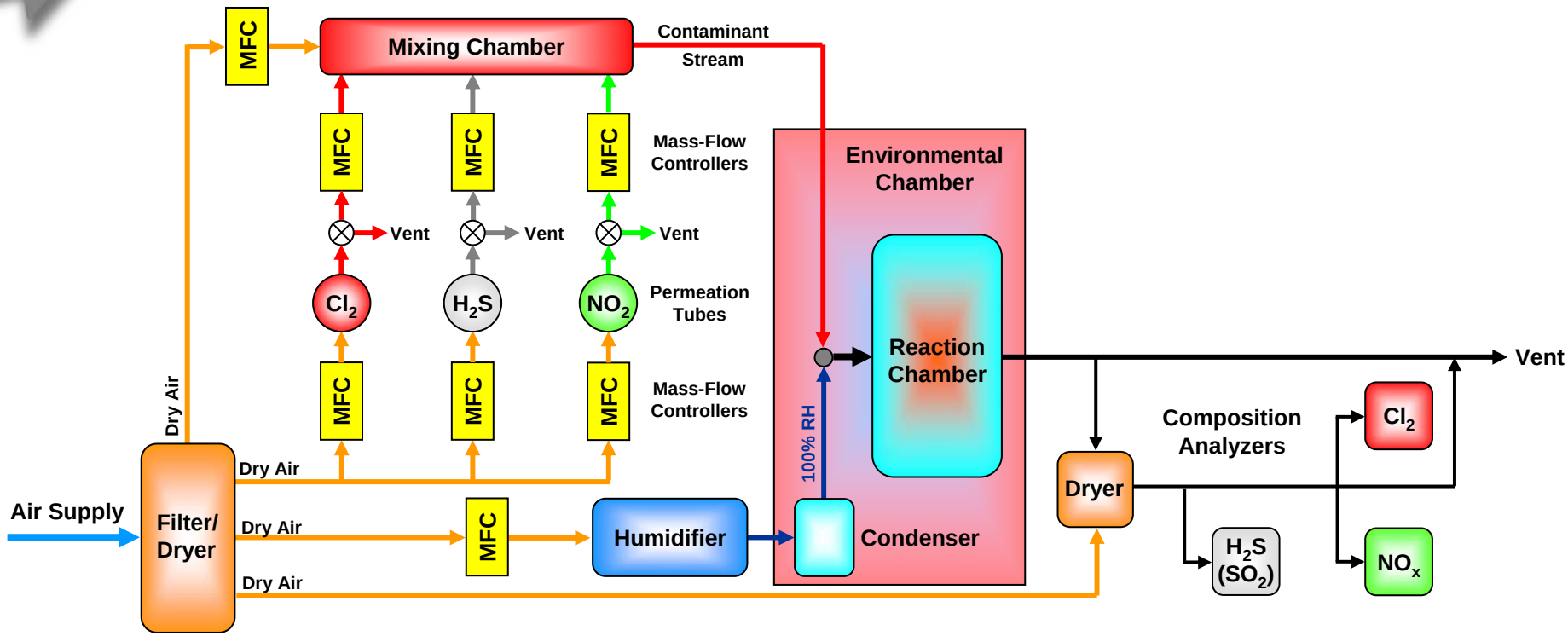
Atmospheric Corrosion Testing Exposure System



- Mass flow controllers and composition analyzers are used to control the environmental conditions via a feedback loop
- Recent system improvements include increased capacity and enhanced compositional analysis by adding ability to measure and control chlorine

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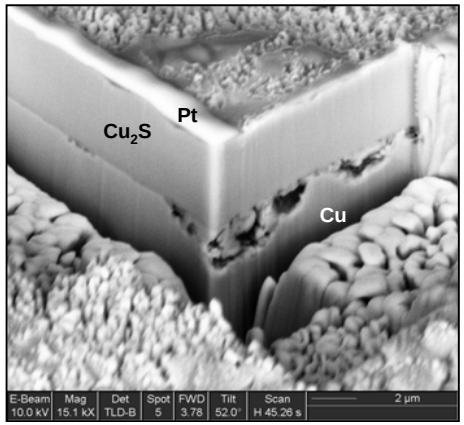
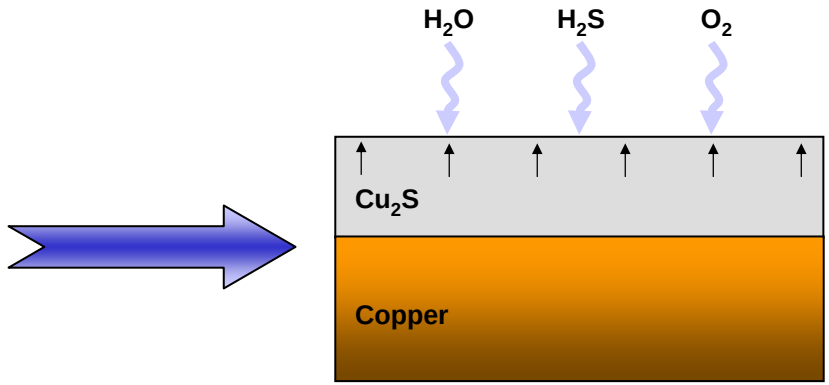
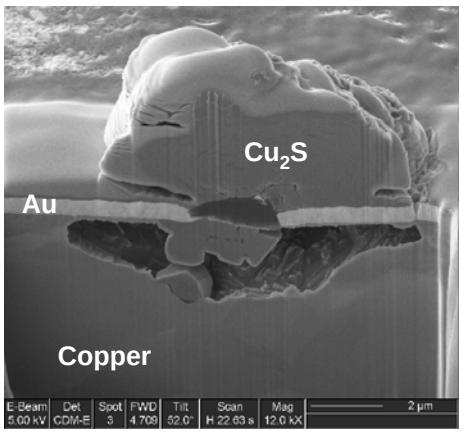
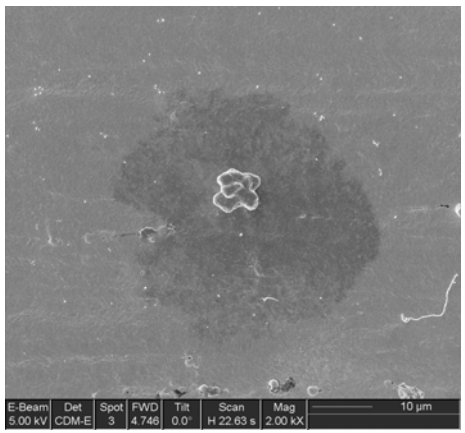
Corrosion Product Morphology

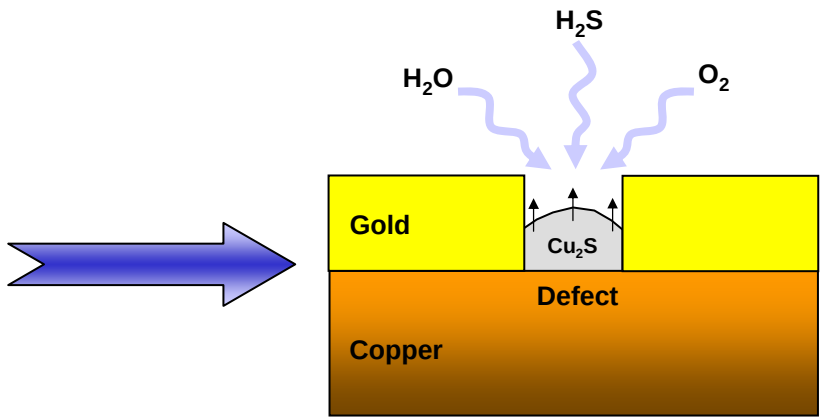
In the case of a bare copper surface, sulfide growth is effectively uniform for the entire exposed surface area.











When an electroplated gold layer is present:

- **Corrosion occurs only at defects in the gold layer.**
- **Sulfidation of copper exposed at the base of defects (pores) in the gold layer results in the formation of sulfide blooms.**
- **The presence of the sulfide corrosion product increases the contact resistance**

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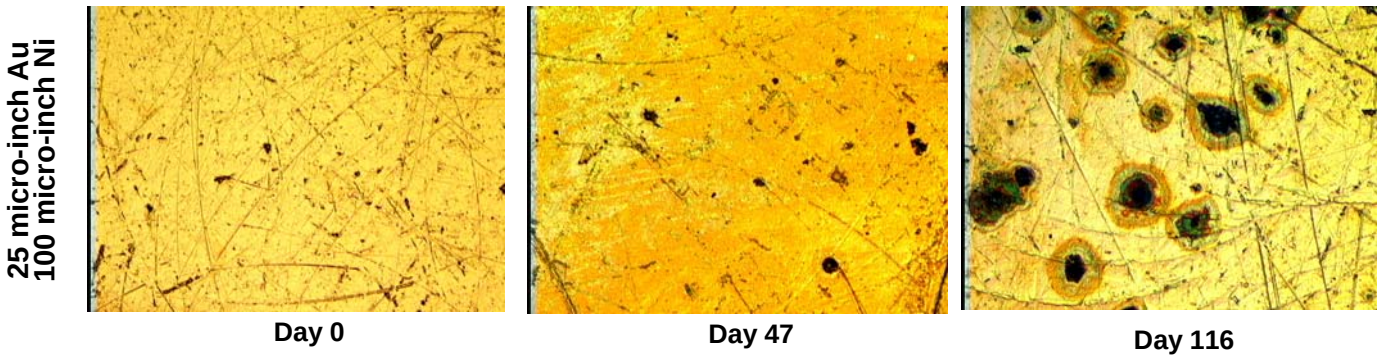
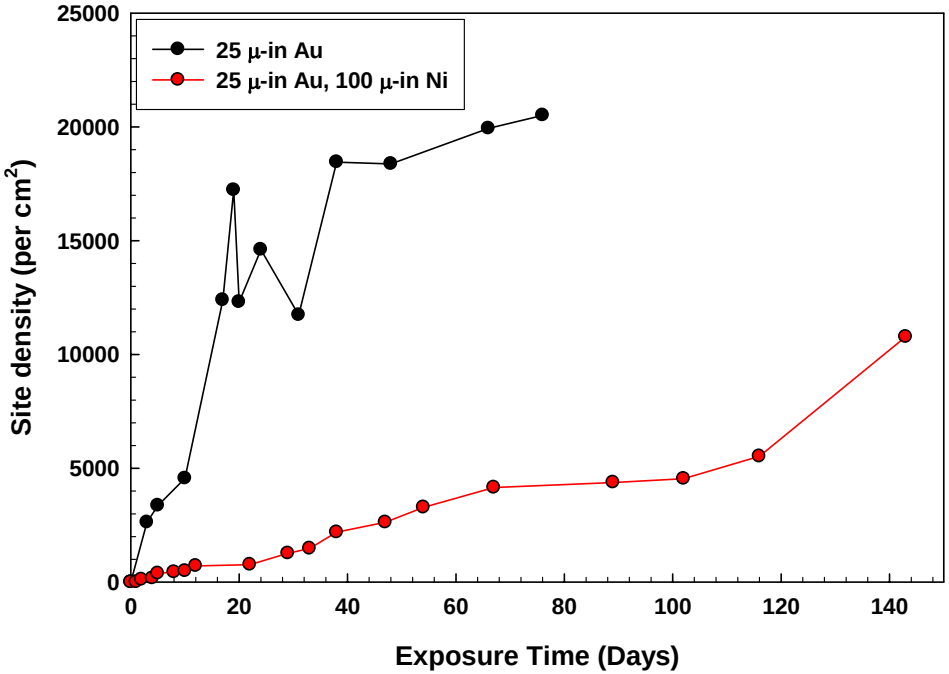
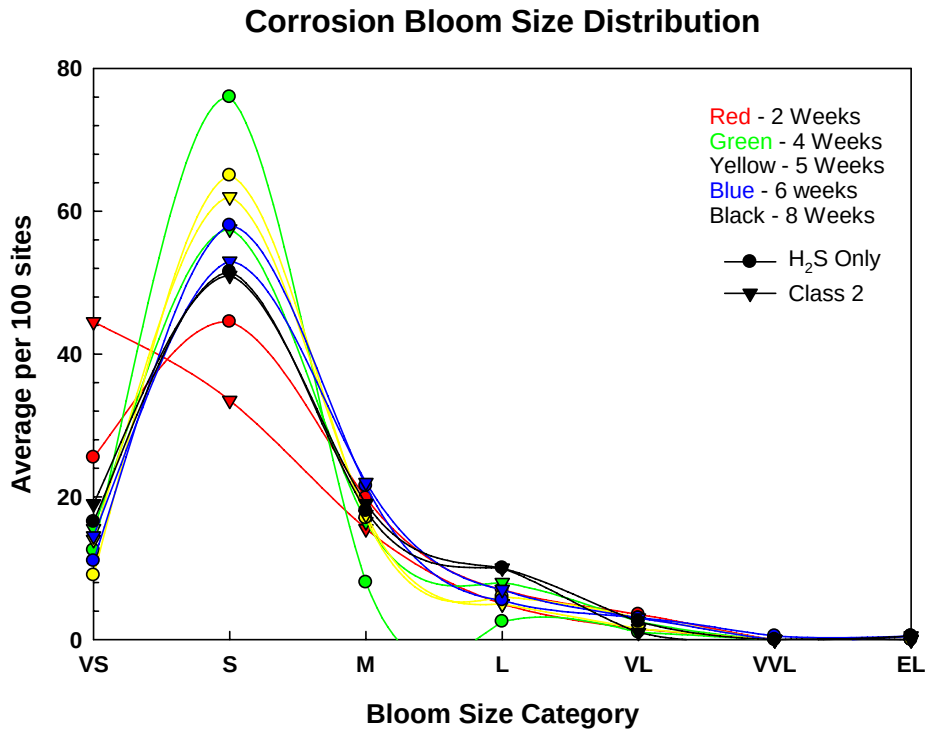
Optical Assessment of Surface Degradation

Optical microscopy is used to visually assess the nature and extent of the damage







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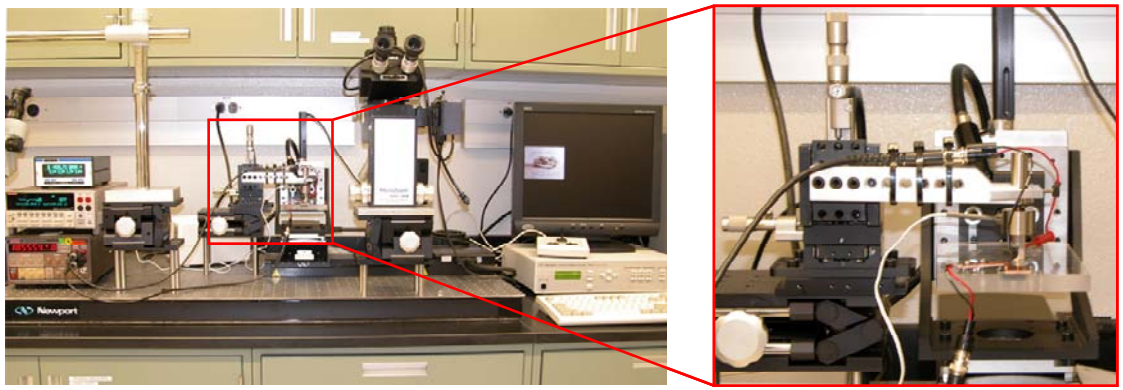
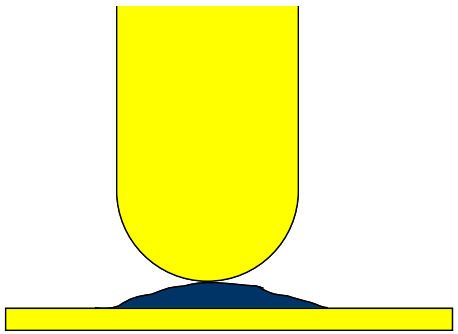
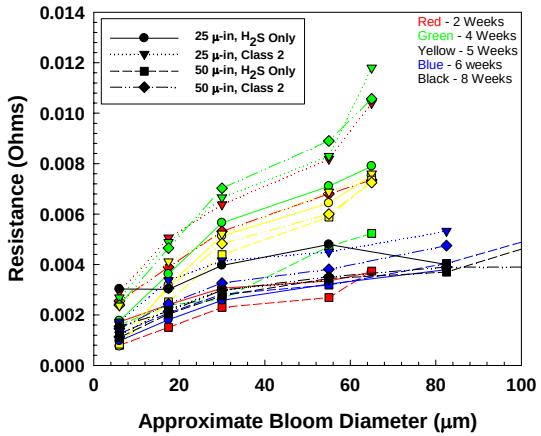
Quantifying the Electrical Properties of the Aged Surface

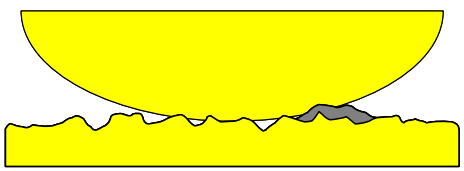




Small probe

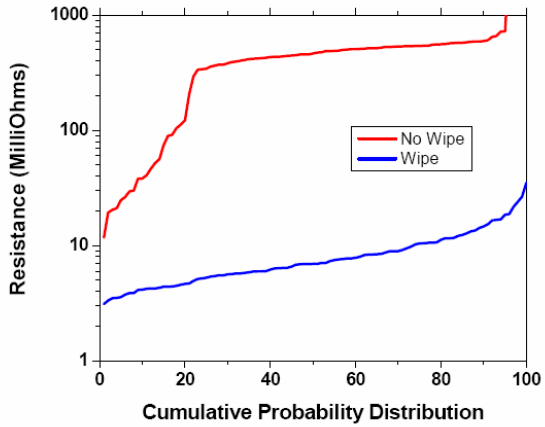
Target individual sites





Large probe

Surface Averaged Response



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Critical Needs for the Model

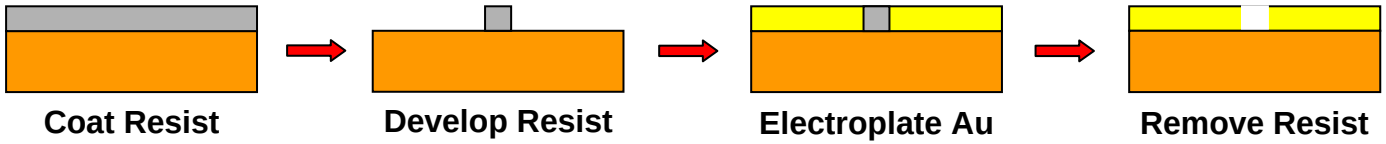
There are a number of key parameters needed by the model which require more thorough analysis

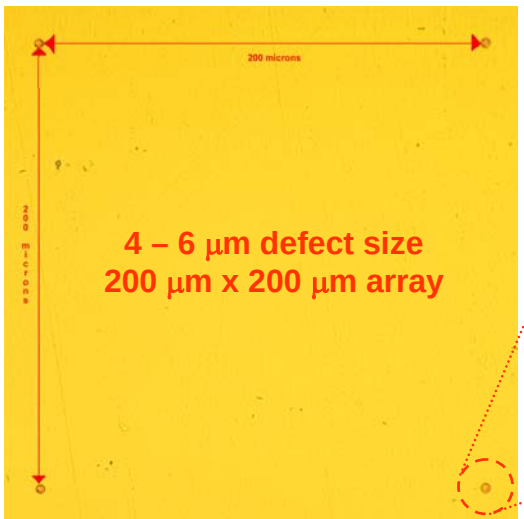
- *Number density of defect sites in the gold layer*
- *Nucleation rate of corrosion sites*
- *Growth properties of corrosion sites*
  - *Growth rate*
  - *Site death*

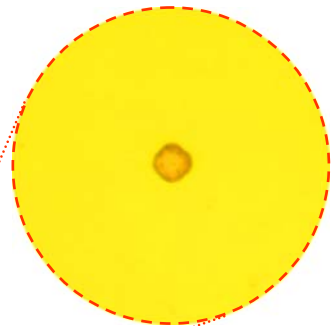
Presently, several techniques are being explored in an effort to fill these gaps

- *Engineered defect structures*
- *Differential Imaging*

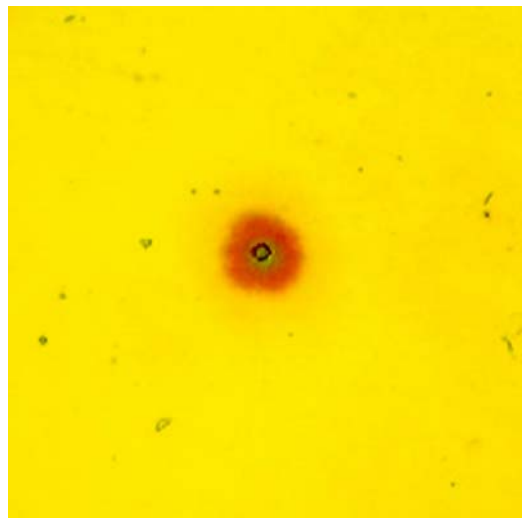
Artificial Defect Structures Used to Assess Sulfidation Kinetics on Gold Plated Copper



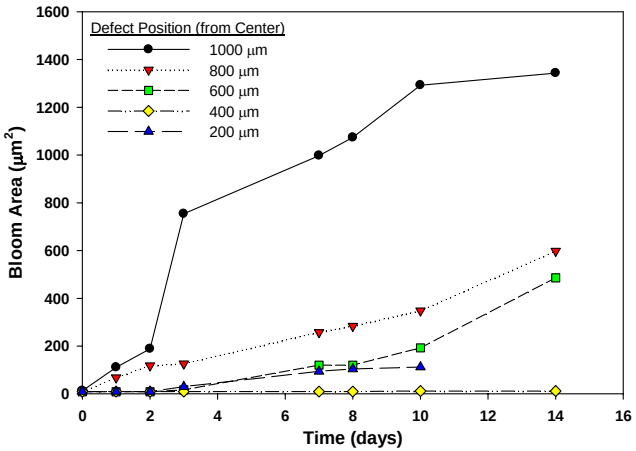




Expose to H_2S atmosphere



Corrosion Product Bloom Size vs. Time



- **Initial design suffered from microloading due to a large fiducial feature**
- **Current design has resolved the microloading issue, but other experimental challenges are still being dealt with**
  - ***Surface preparation***
  - ***Gold deposition***

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New Technique: Differential Imaging

- Differential Imaging is an advanced image analysis technique where a time sequence of images is analyzed by subtracting a baseline image in order to observe changes.
  - Eliminate complications such as an optically complex image (e.g., lots of scratches, etc.)
  - Evaluate *only* the changes in the surface over time
- System consists of the optical system, the exposure chamber, and the analysis software.

Example from Applicable Electronics (post processing software vendor)

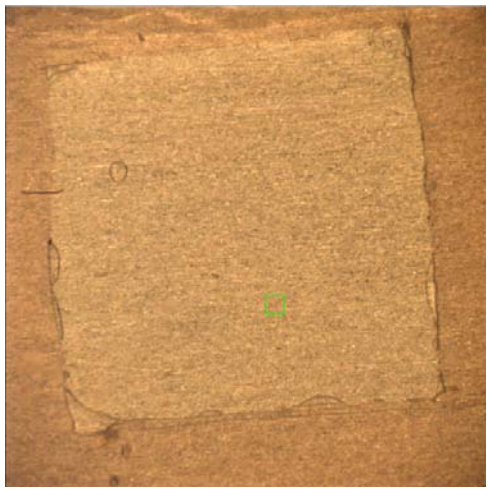
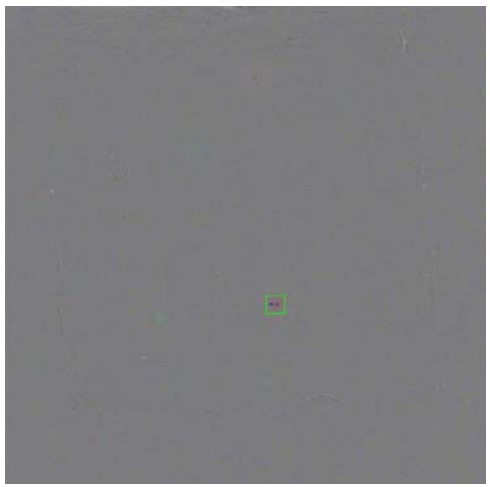
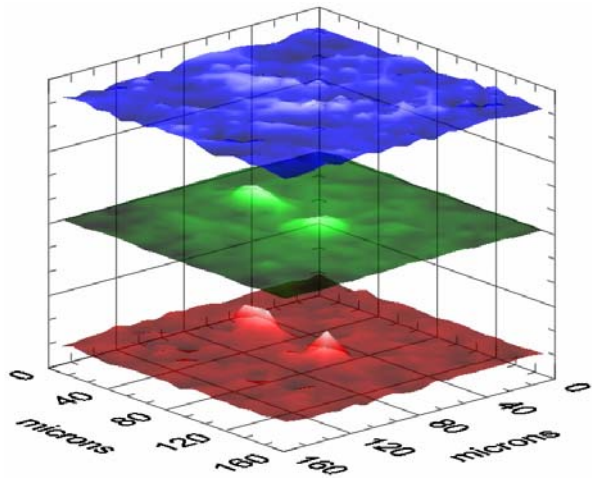


Image of an aluminum surface exposed to a corrosive environment



Same image after subtraction of an image taken two minutes prior – note the corrosion site



Post processing can be used to select the portion of the spectrum which provides the most information

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