

Atmospheric Degradation of Connector Materials

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Dept. 1823 – Corrosion and Electrochemical Science

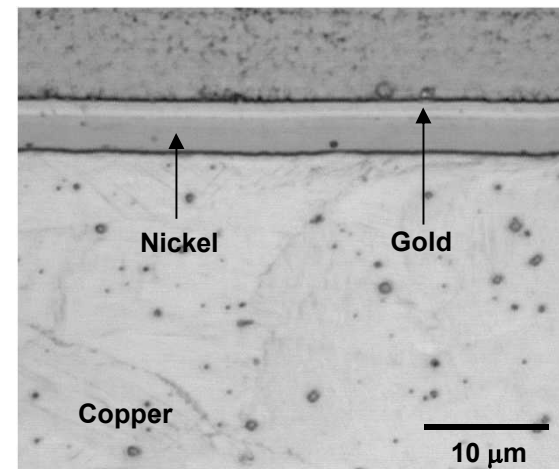
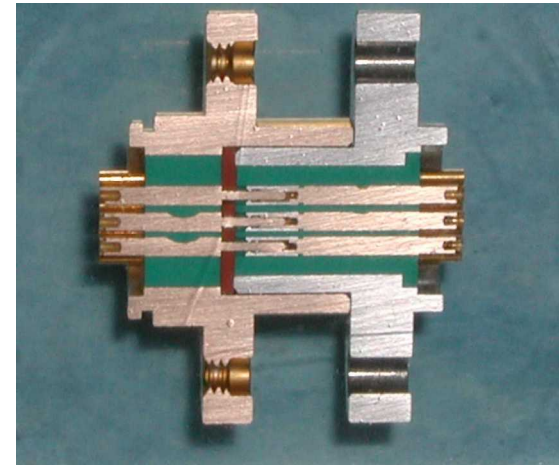
¹Dept. 1514 – Multiphase Transport Processes

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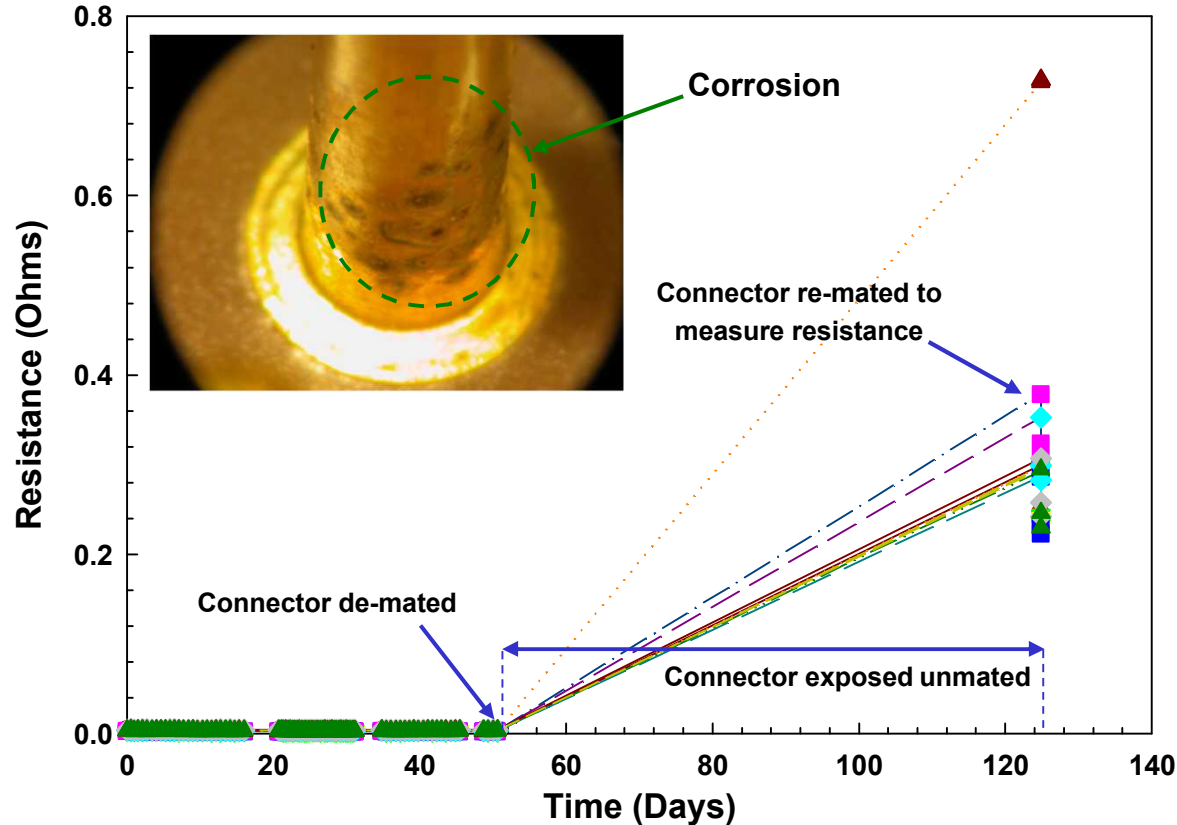
MS&T External Review

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



Electrical Behavior of an Aging Connector

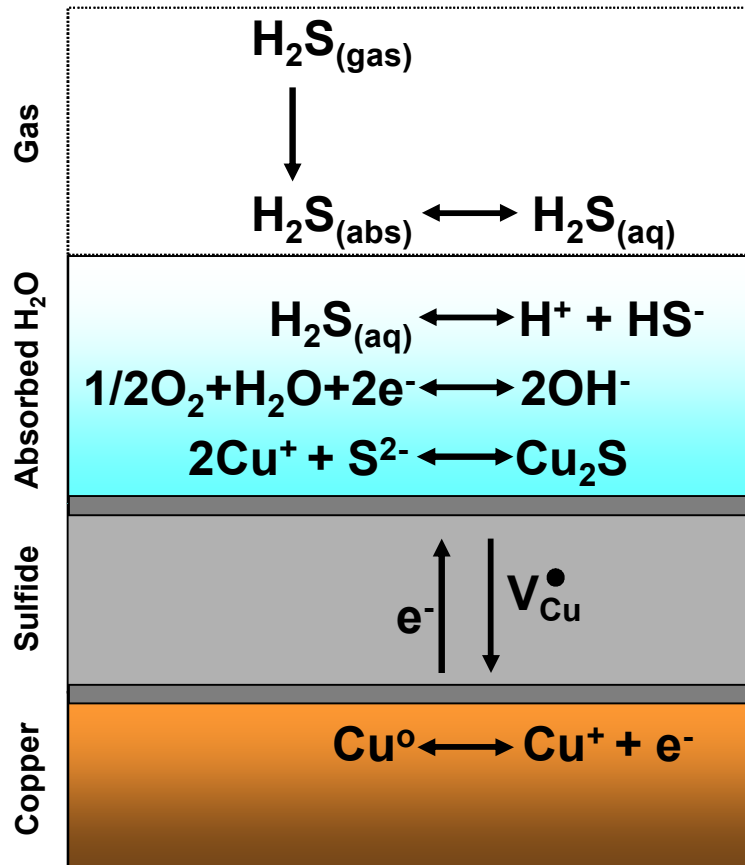


courtesy of
Rob Sorensen, SNL

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.

Copper Sulfidation Kinetics



Sulfide / Atmosphere Interface: Surface Reaction

$$J = k_1 C_{\text{H}_2\text{S}} \exp\left(-\frac{E_{k1}}{RT}\right) - k_{-1} C_{\text{v}-} C_{\text{h}+} \exp\left(-\frac{E_{k-1}}{RT}\right)$$

Sulfide Layer: Vacancy and Hole Transport

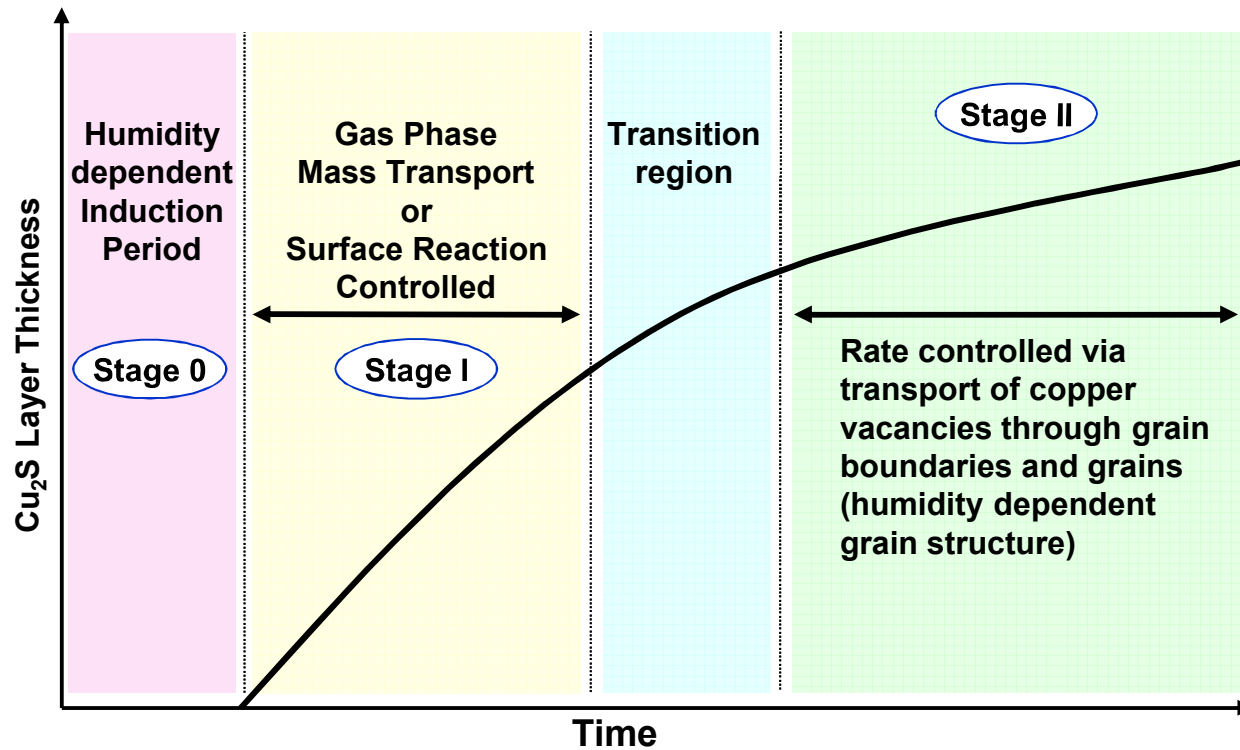
$$2J = D_{\text{oh}} \exp\left(-\frac{E_{\text{Dh}}}{RT}\right) \frac{dC_{\text{h}+}}{dy}$$

$$2J = D_{\text{ov}} \exp\left(-\frac{E_{\text{DV}}}{RT}\right) \frac{dC_{\text{v}-}}{dy}$$

Copper / Sulfide Interface: Surface Reaction

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

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.

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*
 $r_{pore} < r_{pore} < r_{pore}$

*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

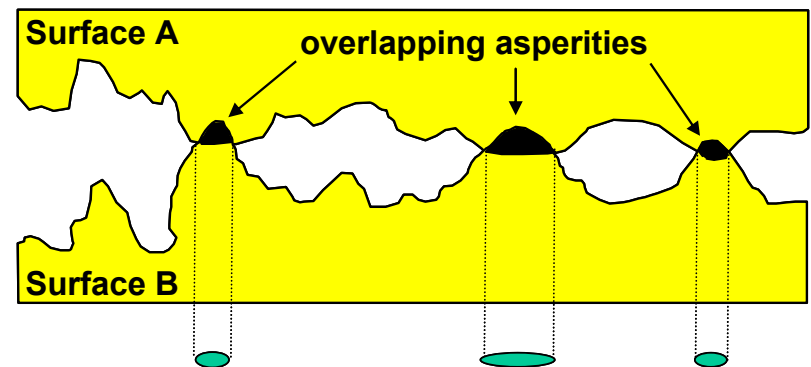
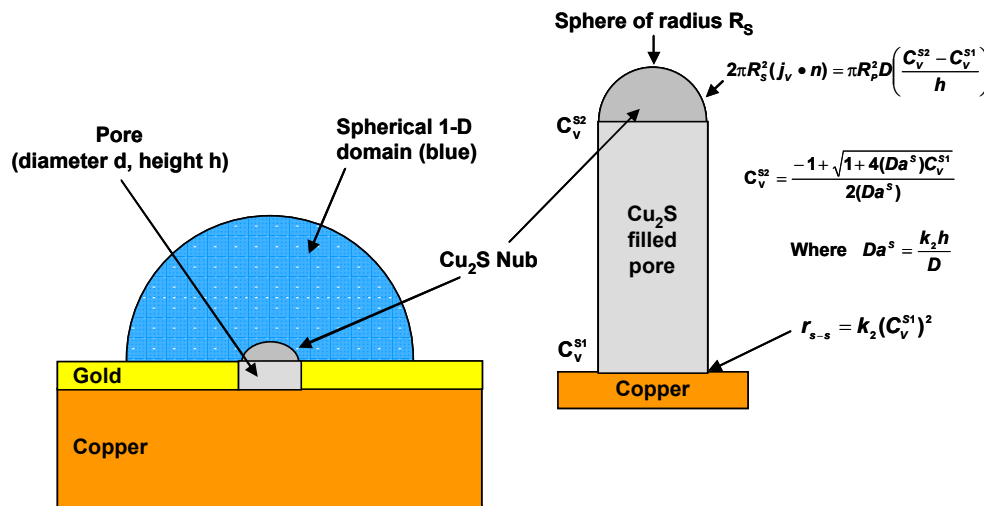
*Cumulative probability
distribution of contact
resistance as a function of
time and environmental
conditions $CPD(t)$*



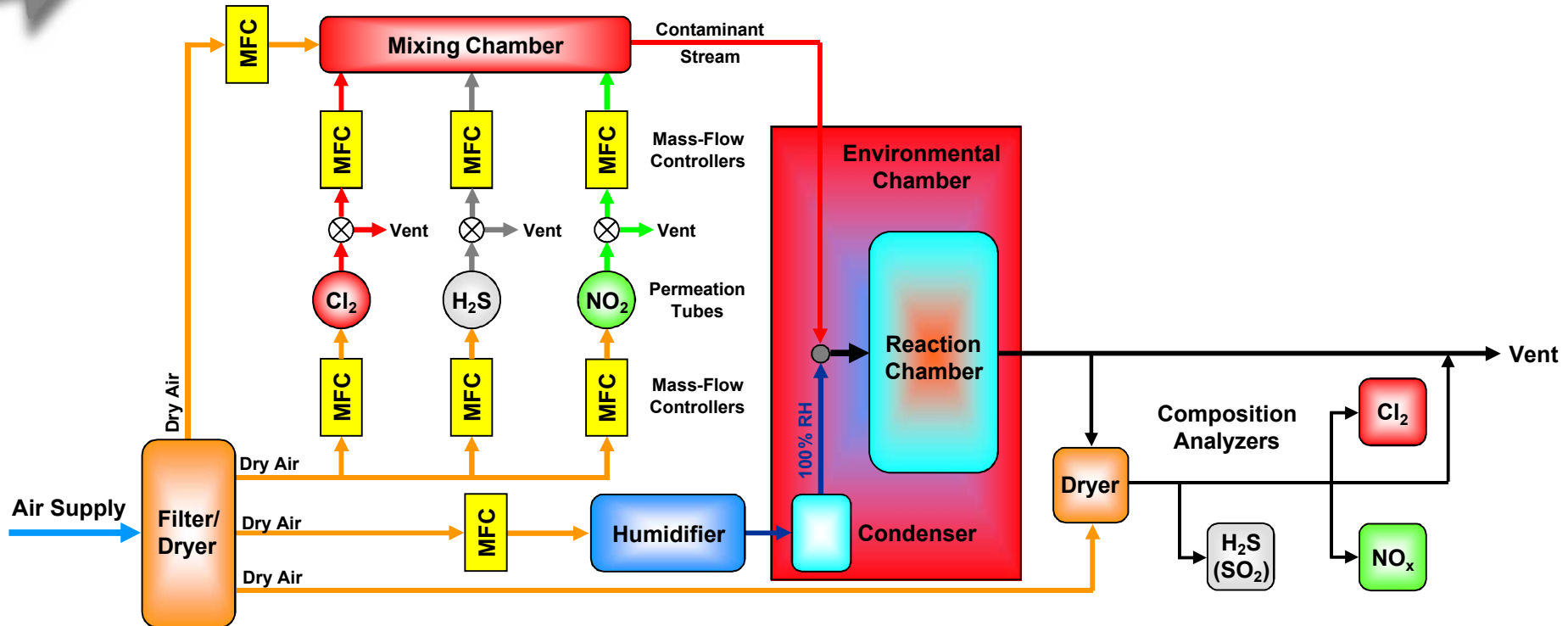
Modeling the contact surface requires that small scale features be accurately captured

- Modeling the sulfidation process and its 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)



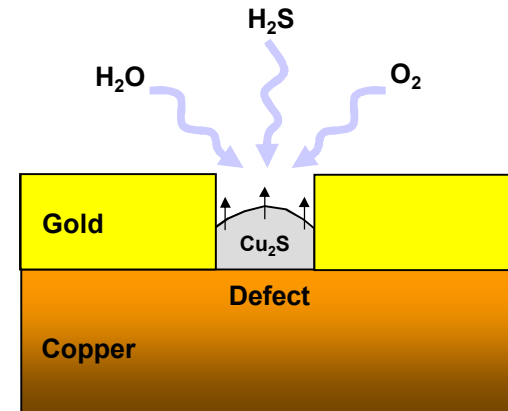
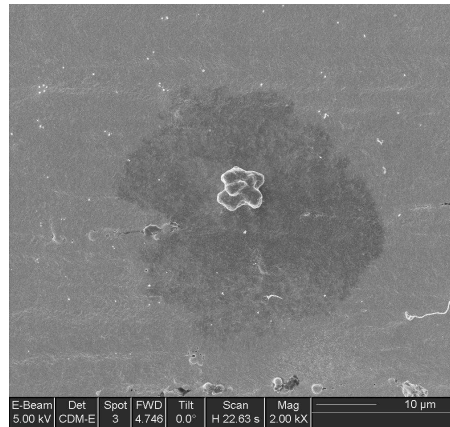
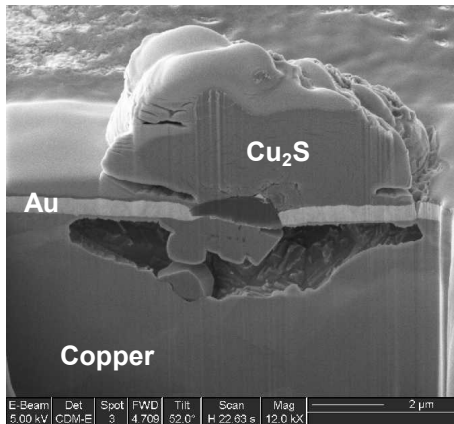
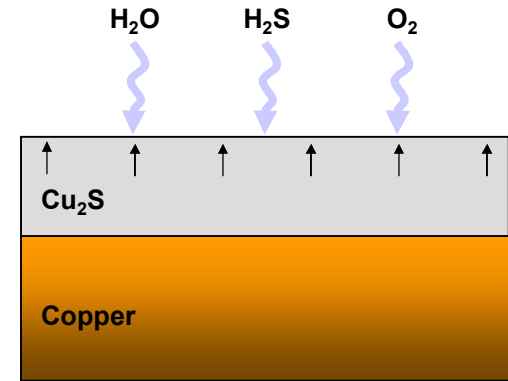
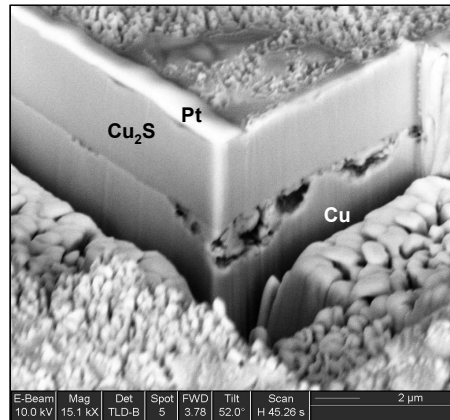
Atmospheric Corrosion Testing Exposure System



- 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

Corrosion Product Morphology

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



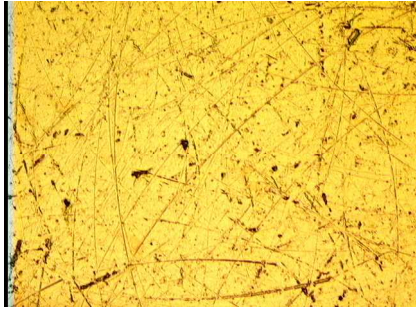
When an electroplated gold layer is present:

- 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

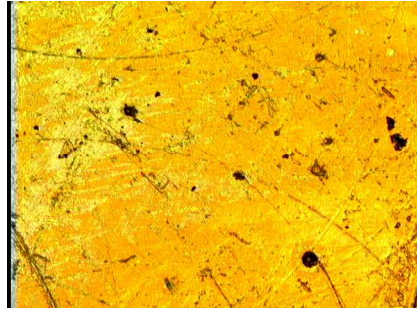
Optical Assessment of Surface Degradation

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

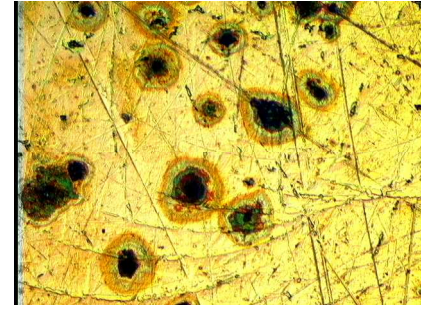
25 micro-inch Au
100 micro-inch Ni



Day 0

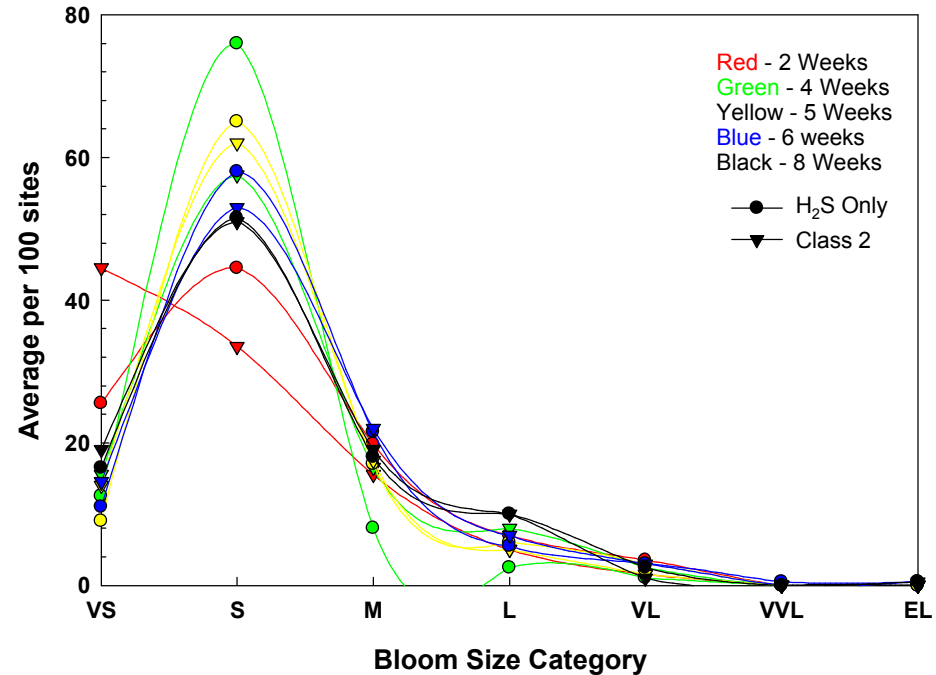
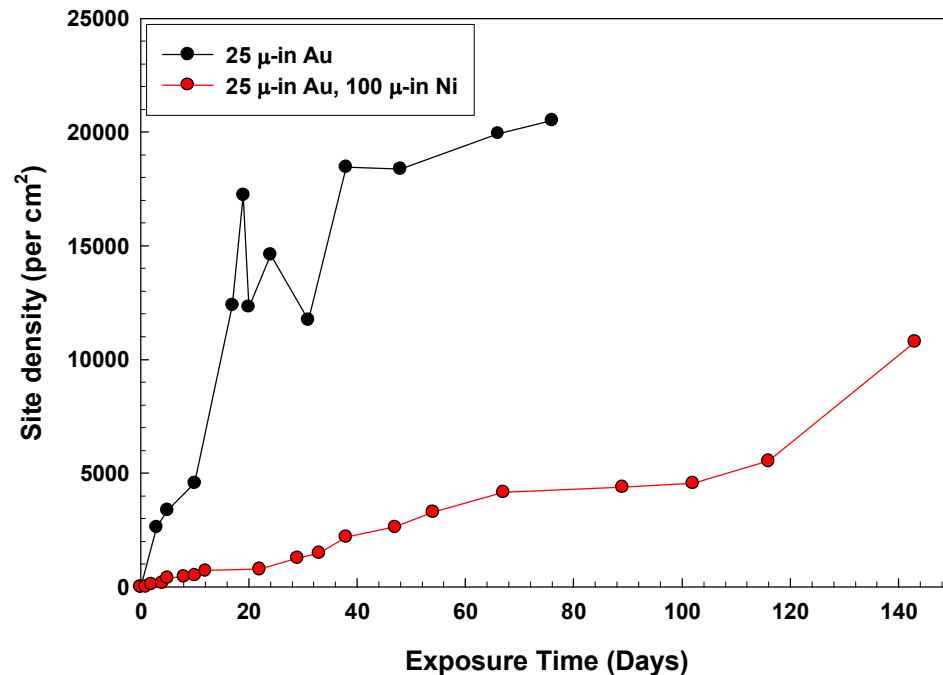


Day 47

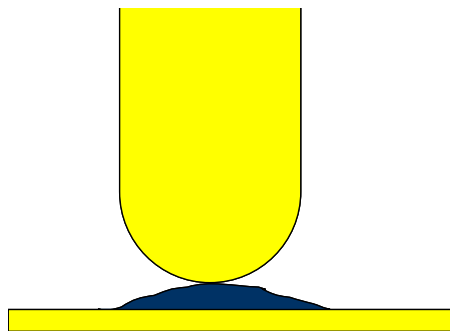
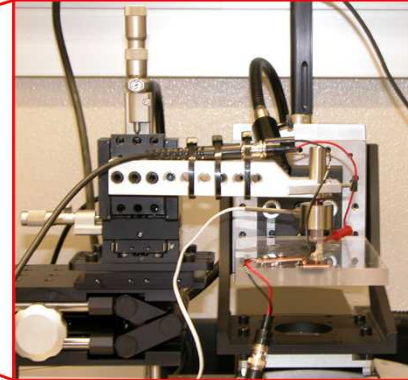
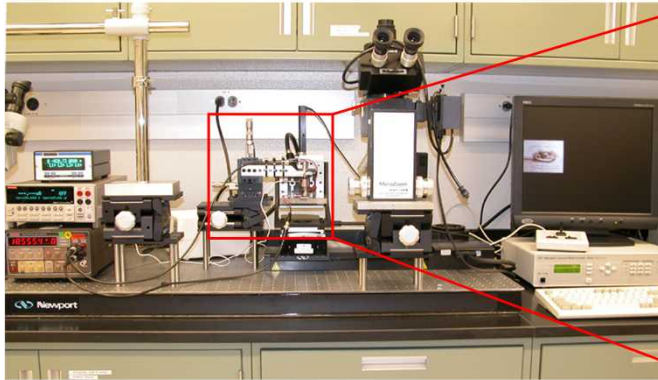


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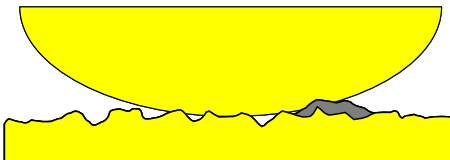
Corrosion Bloom Size Distribution



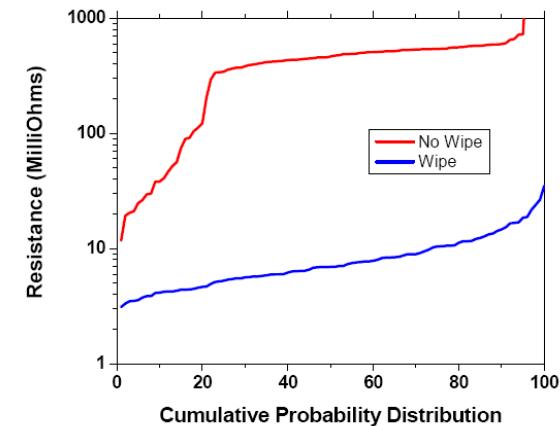
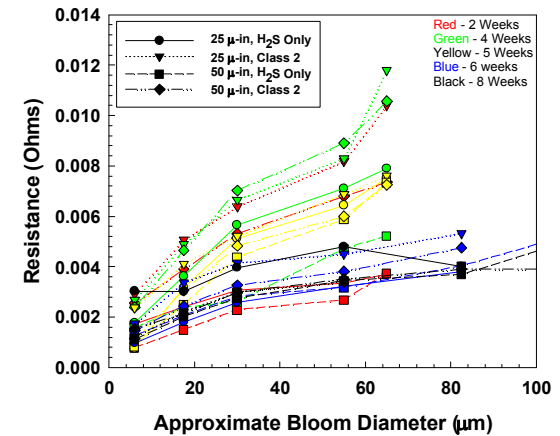
Quantifying the Electrical Properties of the Aged Surface



Small probe
→
Target individual sites



Large probe
→
Surface Averaged Response





Critical Needs for the Model

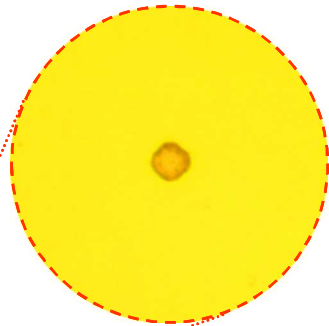
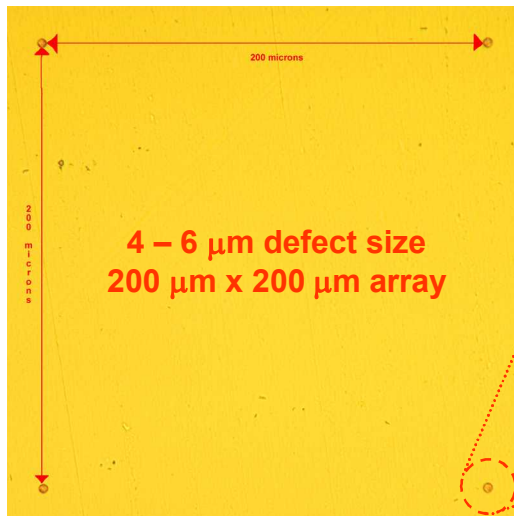
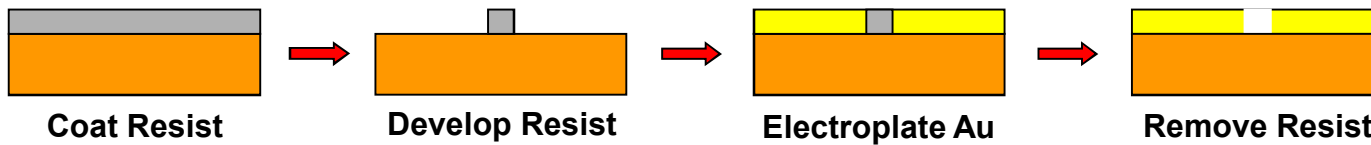
There are a number of key parameters needed by the model which require more thorough analysis

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

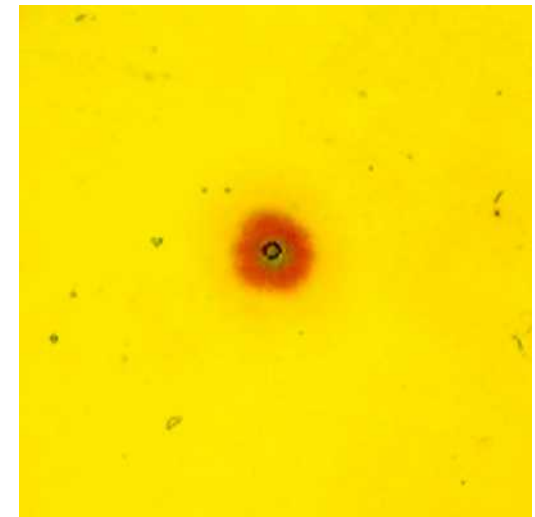
Presently, several techniques are being explored in an effort to fill these gaps

- *Engineered defect structures*
- *Differential Imaging*

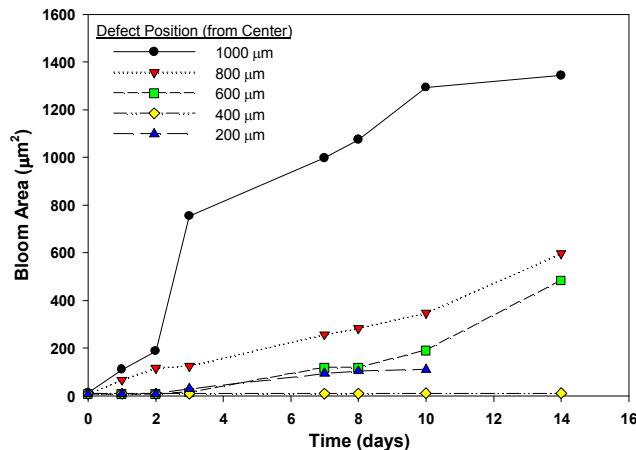
Artificial Defect Structures Used to Assess Sulfidation Kinetics on Gold Plated Copper



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*

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)

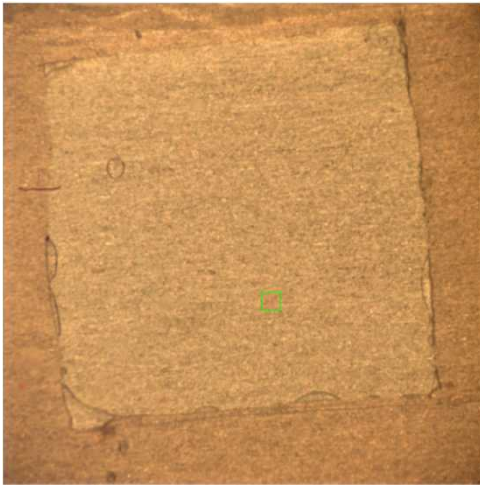
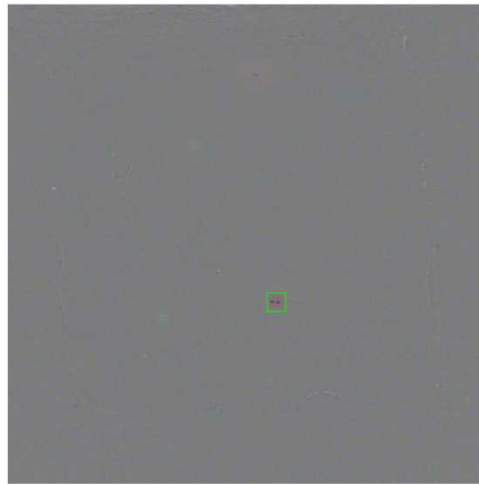
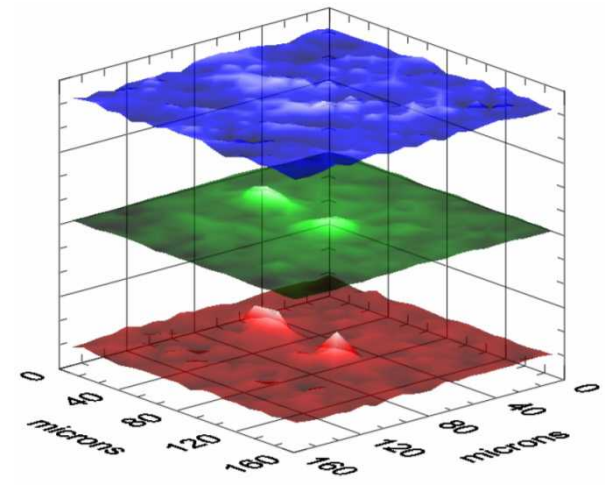


Image of an aluminum surface exposed to a corrosive environment



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



Impact + Future directions

Programmatic Impact

- Project output to date assisted with the selection of an appropriate metallization (MIL spec vs. COTS) for W76-1 micro-miniature connectors
- Model will enable qualitative assessment of component life as a function of the materials of construction and environmental parameters
- New analysis techniques will allow detailed evaluation of atmospheric corrosion processes
- Investment in atmospheric corrosion testing capability will enhance the performance of many other projects (SFI investigations, failure analyses, materials assessments, etc.)

Future Direction

- Complete update of atmospheric corrosion test facilities
- Complete test matrix evaluating impact of substrate material, pre-plating surface finish, and plating deposit morphology on atmospheric corrosion performance of connector materials
- Determine the remaining kinetic parameters and validation of the corrosion model