# Molecular Modification of PCB Substrates for Fine Line Patterning

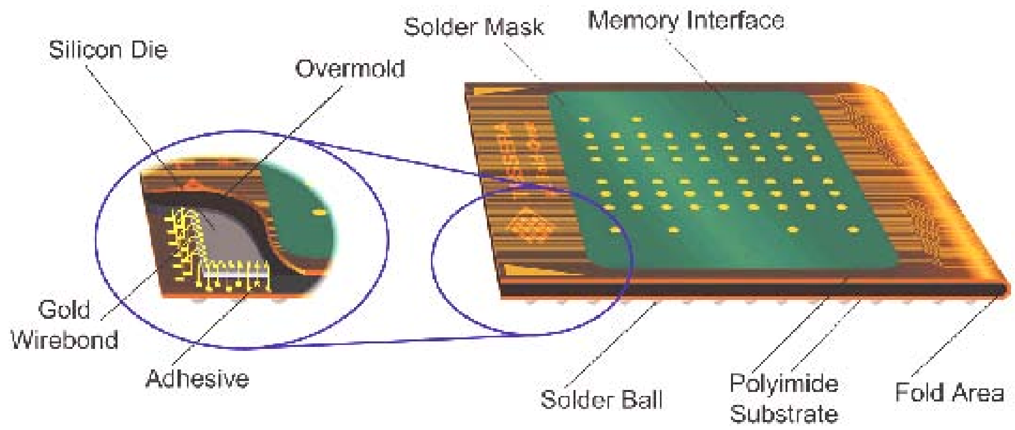
**Werner G. Kuhr, Ph.D.**
**Founder and Vice President, Research**
**ZettaCore, Inc.**
**369 Inverness Drive, Suite 350,**
**Englewood, CO 80112 USA**
**Werner.Kuhr@zettacore.com**

Presented Wednesday, Sept. 9, 2009
IEEE Santa Clara Valley Chapter, CPMT Society
www.cpmt.org/scv

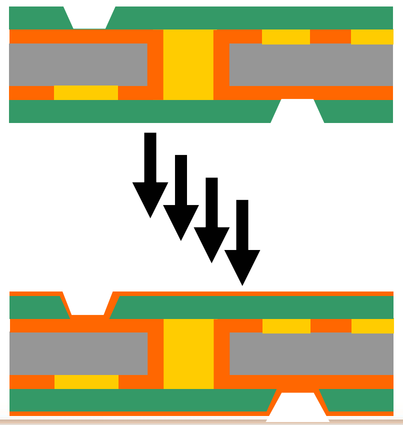
# Next Generation IC Packages

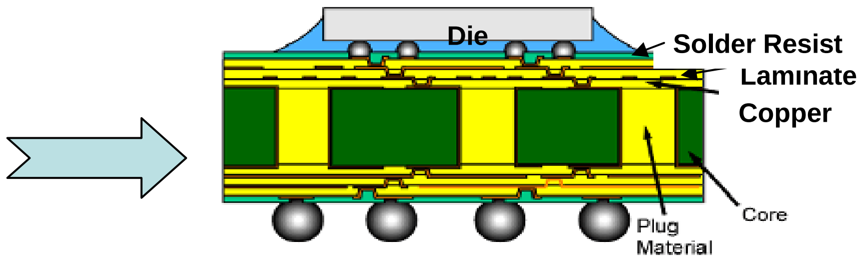
ZETTACORE

Goal: Multilayer PCB substrate with ~10 micron L/S




Process: Semi-additive (plating and build-up lamination)






*Microprocessor package*

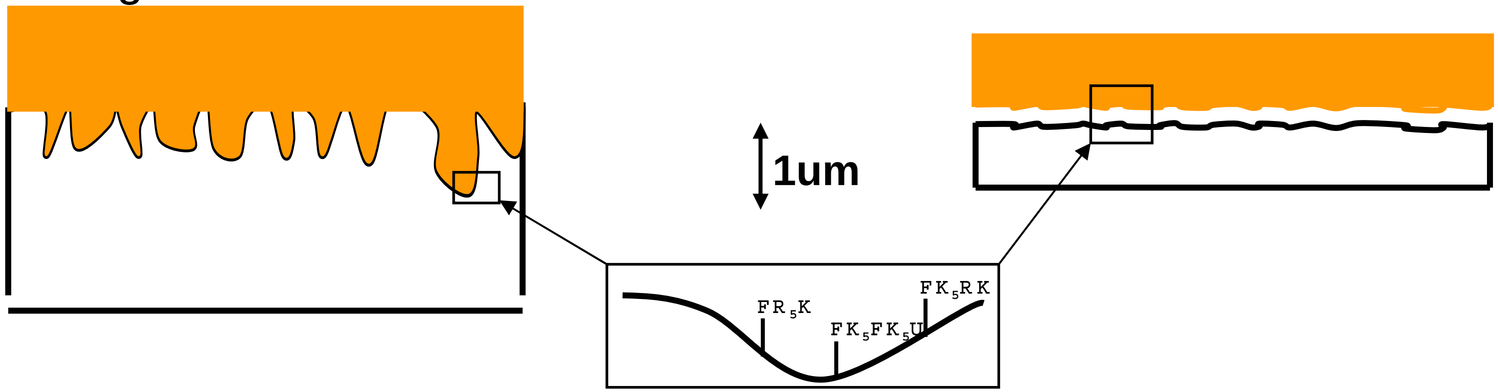
# Adhesion Issues in Substrates

- Fine line patterning (< 25 um) requires smooth surface
  - Semi roadmap requires ~10um line/space on substrates in 3-5 years
  - Mechanical adhesion insufficient for reliability of fine line traces

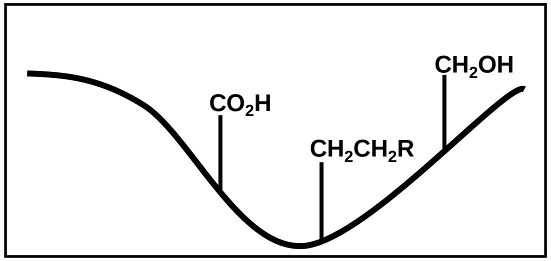
- Adhesion mechanism for fine lines will depend on mechanical and chemical forces

Existing Approach
Roughened surface

New approach
“Smooth” surface



# Improving Adhesion in Substrates



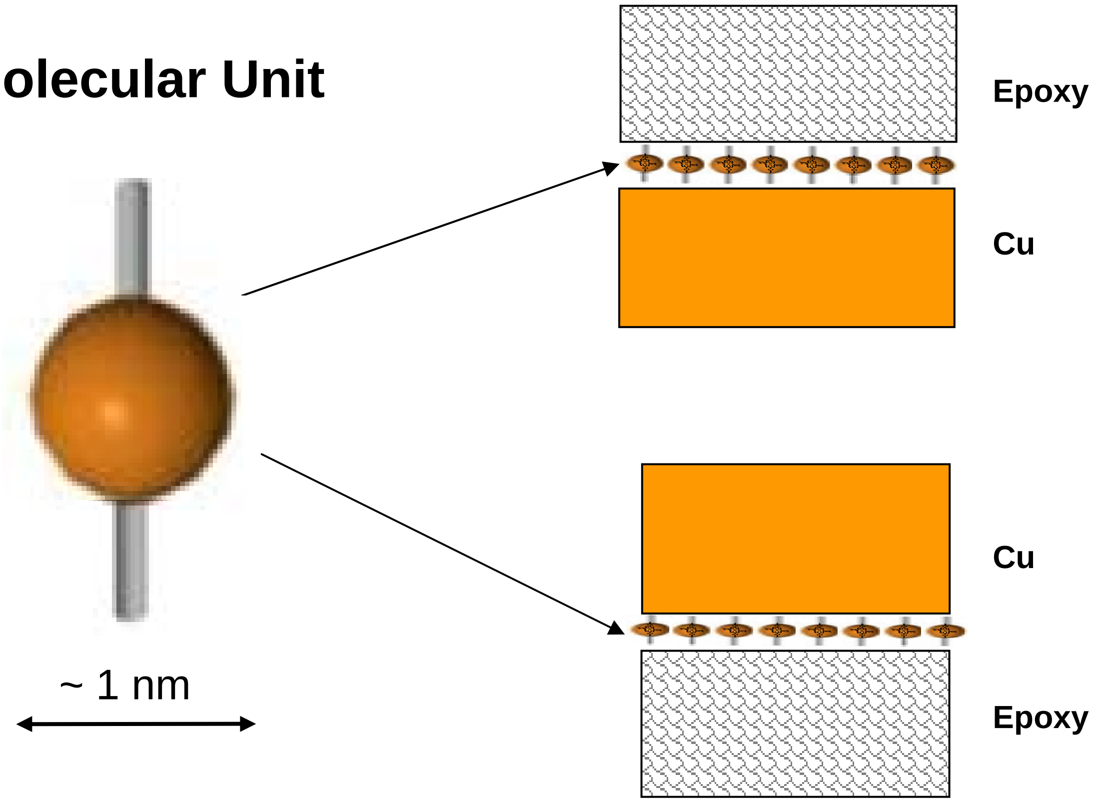

- Chemical composition of surface depends on many factors
  - Material composition
  - Curing conditions
  - Storage history
  - Chemical treatments (cleans, desmear, etc.)

- Selection of adhesion chemistry
  - Stable chemistry (i.e., good shelf life, reproducibility)
  - Wide process window (time, temperature, concentration)
  - Broad application to many substrates

# ZettaCore Approach: Molecular Interface

ZETTACORE

## Molecular Unit

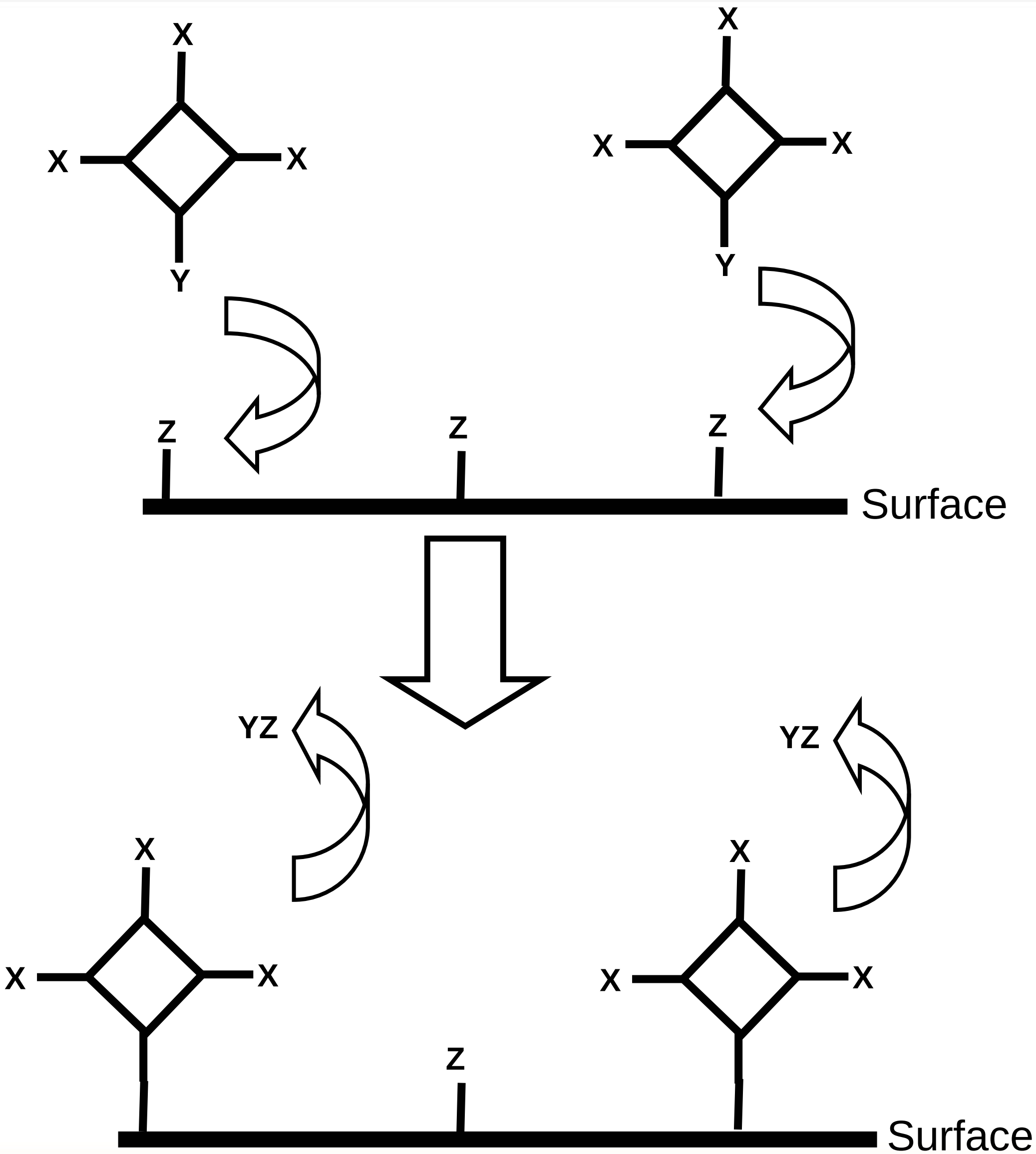



- Molecules can attach “incompatible” materials
- Copper can be attached to epoxy
- Epoxies, resists, etc. can be attached to copper
- Chemistry engineered for specific material properties

# Summary of ZettaCore feasibility studies

- Porphyrin molecules have survived exposure to various electroplating solutions
  - Cu plating demonstrated on a variety of substrates
  - Enhanced peel strength correlates with good porphyrin coverage
- Porphyrin survives Cu metal deposition
  - Porphyrin configuration does not change significantly in Cu film
  - Metal structure of Cu film on top of porphyrin monolayer is as smooth as underlying Si (100) structure

# ZettaCore Chemistry: Initial Work




X: Cu, Pd-binding component

Y: Surface reactive component

Z: Surface leaving group

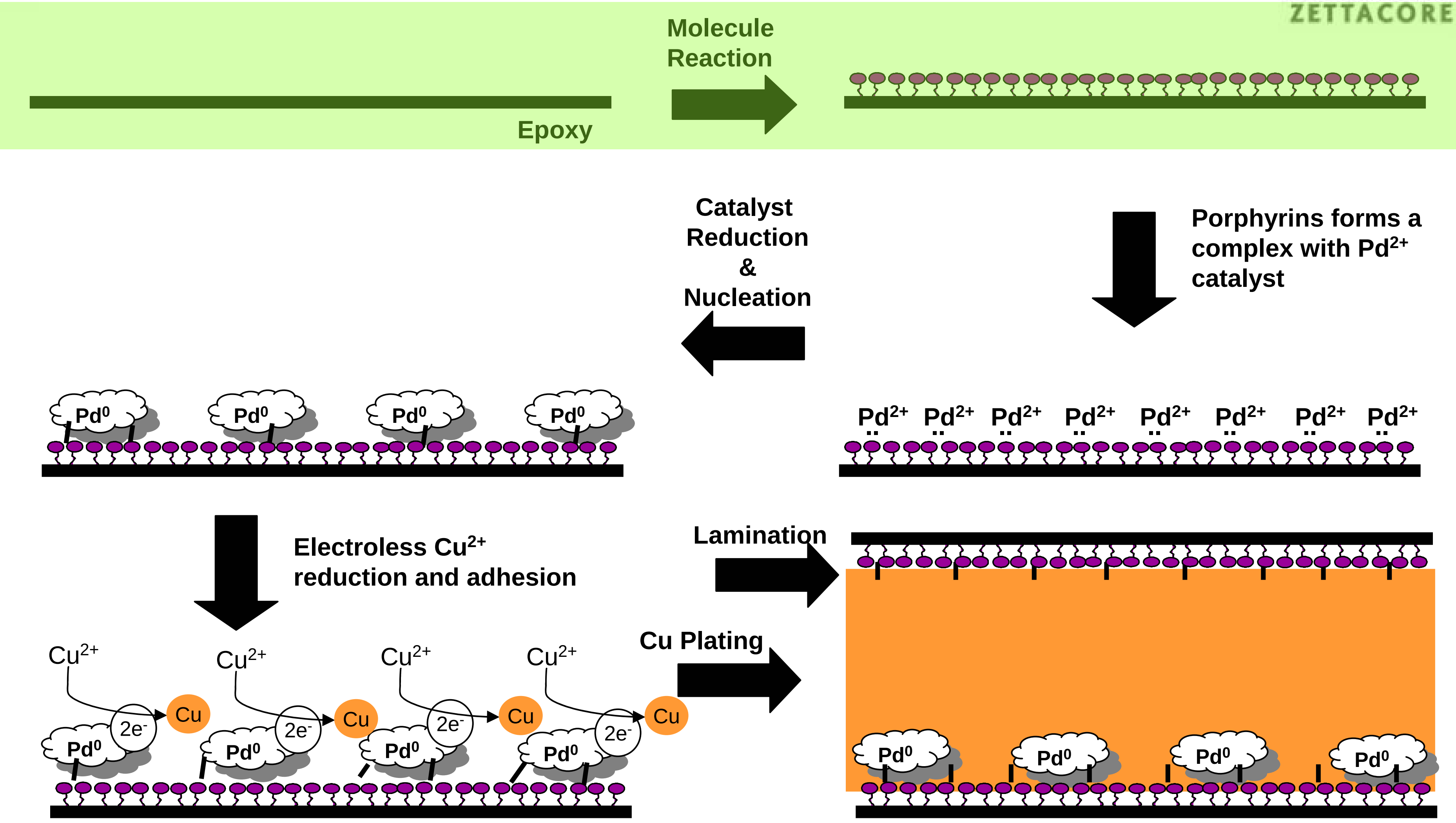
# Molecule / Process Development

ZETTACORE

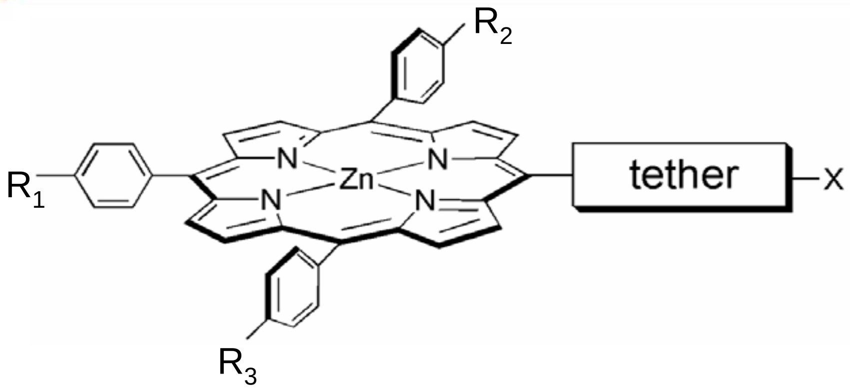
- Identification of reactive components
  - Chemical characterization of target substrates
  - Identification of reactive chemical species on surface
- Molecular design and synthesis
  - Design of reactive intermediates for attachment to selected surface
  - Id or synthesis of desired molecules and chemical characterization
- Molecule attachment and characterization
  - DOE on attachment conditions (time, temperature, concentration)
  - Method development for surface characterization
- Copper deposition / Lamination evaluations
  - Electroless plating / Electroplating

    - or -
  - Lamination

# Overview: Molecule-enhanced $Cu^{2+}$ plating



# Molecule Optimization




**R for carbon substrates**

Numerous C-C linkages can be formed with existing chemistries

**X for Cu substrates**

Numerous chemistries tested and available for use

- Utilize a stable molecular platform
- Each site can perform different function
  - Individually optimized for specific function
  - Failure analysis possible for each function
- Systematic building block approach
  - Isolate the chemistry needed for specific function
  - Each site can be optimized independently and systematically
- Allows root cause failure analysis and complete characterization
  - Allows rational design and optimization of each molecular component
  - Preserves flexible design that can be modified & optimized as conditions change

# ZettaCore MI Process for Cu Plating

ZETTACORE

**Molecule Attachment**

Substrate Cleaning → Molecule Deposition → Baking Attachment → Rinse & Post Treatment

**E-less Cu Plating**

**Pre-anneal**

## Standard Chemistries Employed

No need for changes in standard processes!!!

**Electrolytic Cu Plating**

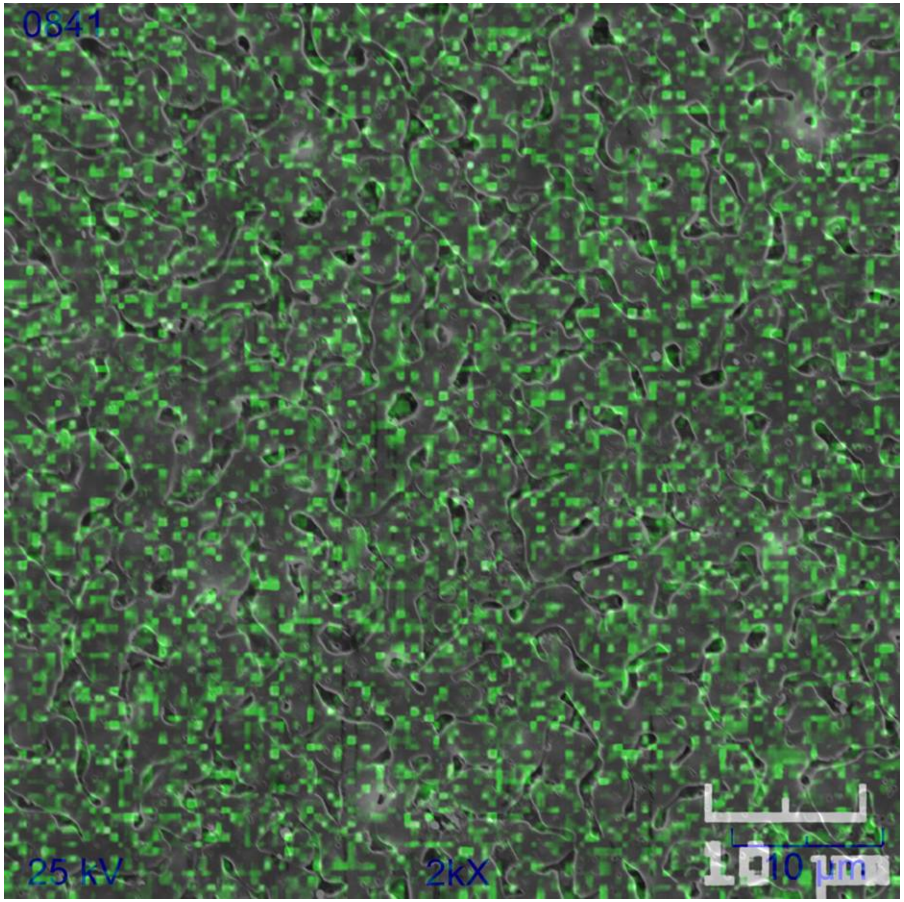
**Post-anneal**

**Testing**

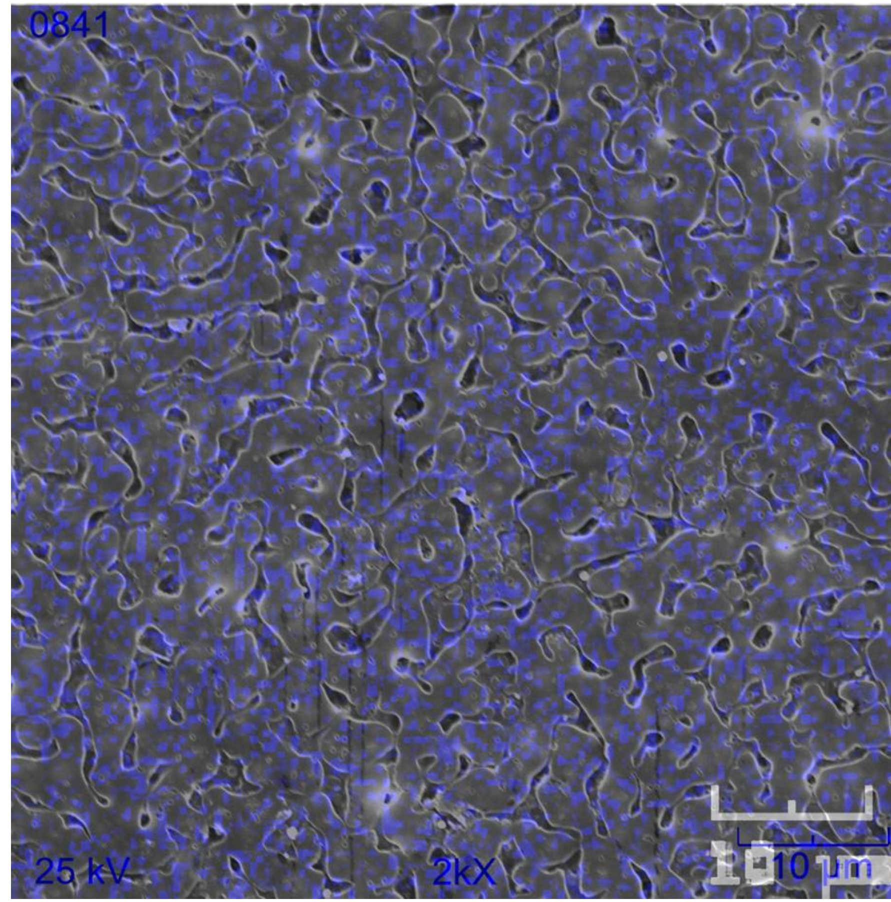
Peel Strength Test → HAST → Repeat Peel Test

# Correlation of porphyrin and Pd distribution on surfaces

Porphyrin distribution




Pd distribution




- Porphyrin molecules distribute uniformly on the epoxy surface
- Pd catalyst distributes uniformly on top of porphyrin

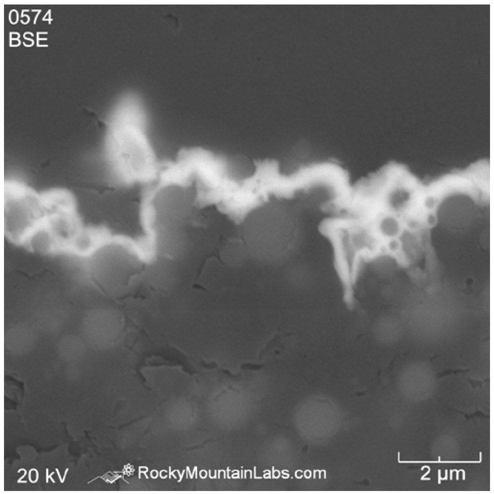
# Cross-sectional SEM of E-less Cu deposition

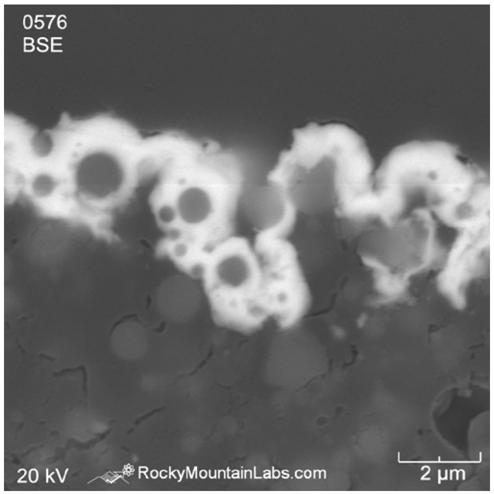
ZETTACORE

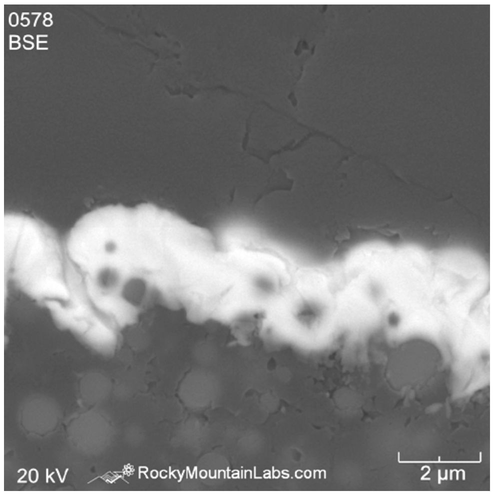
Eless-Cu: @ 30°C

10min. | 20min. | 40min.

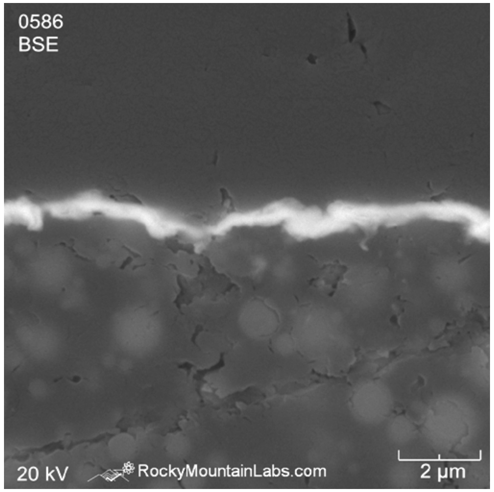
Roughened surface

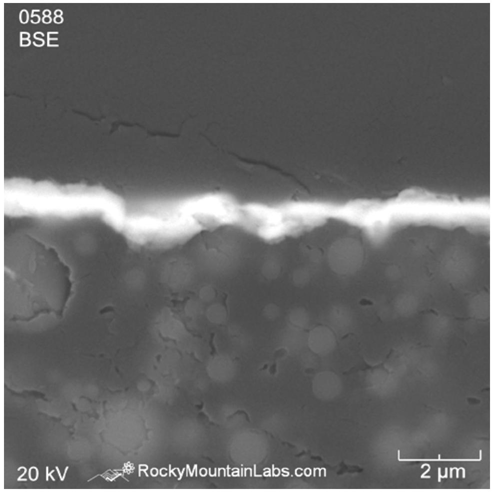


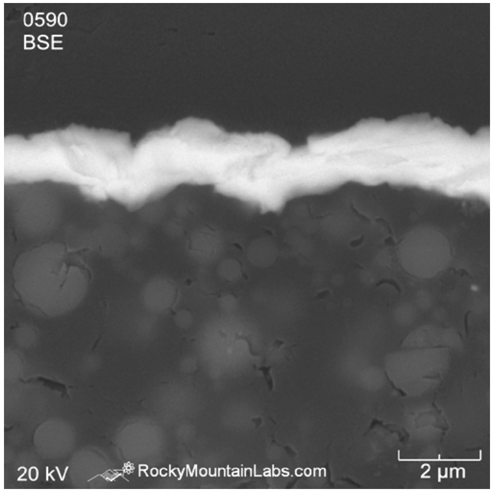



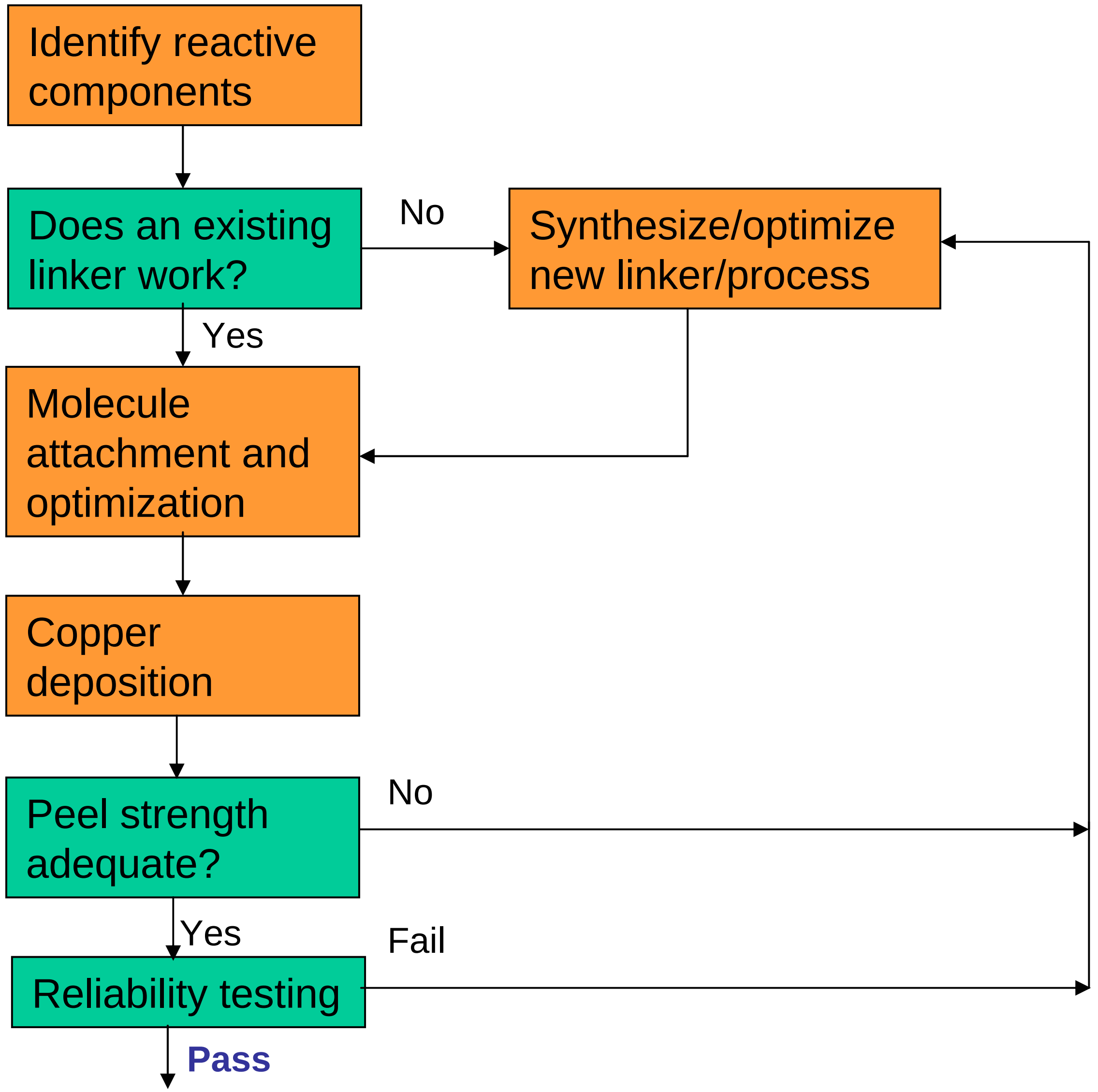

Porphyrin attached smooth surface



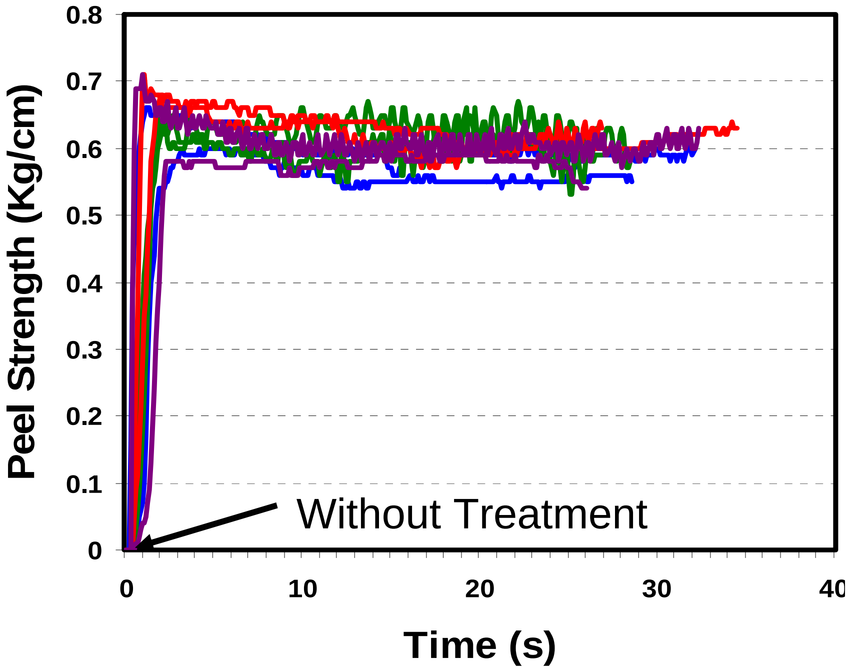
# Optimization of Molecule Properties



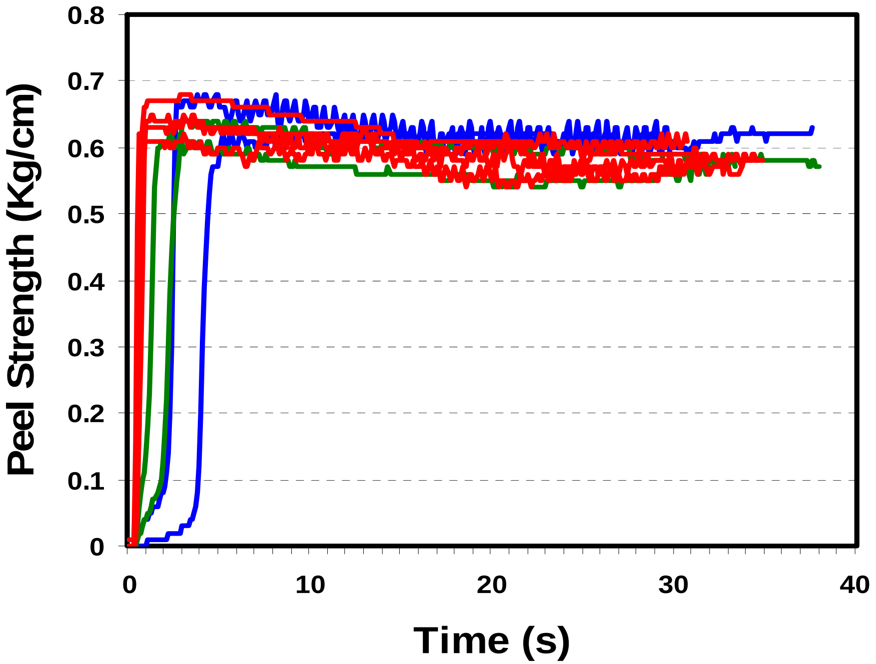
# Demonstration of Peel Strength on Planar Substrates

ZETTACORE

**Smooth substrate**
**0.62 ± 0.02 Kg/cm**




**Roughened control**
**0.60 ± 0.02 Kg/cm**




- Demonstration of peel strength pre-HAST testing
  - 0.62 ± 0.02 Kg/cm on smooth surface, better than roughened control

# Summary: Impact of Molecular Layer for Copper on Epoxy – Reliability Tests

ZETTACORE

| Test | Test conditions | Success criteria | Result /Status |
|---|---|---|---|
| Peel strength | Peel width 1.0 cm, speed 5.0 cm/min at 90 degree angle | Roughened control (~0.6 Kg/cm) | 0.62 Kg/cm |
| Reflow and HAST | Pre-conditioning (Level 3): 125C – 25 hr, 30$^{o}$C/60%RH – 192 hr<br>Reflow: 260$^{o}$C 3 times<br>HAST: 130$^{o}$C, 85%RH – 96 hr | Peel strength degradation $\leq$ roughened control | 10% degradation vs. 13% for roughened control |
| Extended Bake | 165$^{o}$C – 504 hr | Peel strength degradation $\leq$ roughened control | No degradation |
| Thermal Cycle | Pre-conditioning (Level 3)<br>Reflow: 260$^{o}$C 3 times<br>TC (cond. C): -65$^{o}$C to 150$^{o}$C, dwell 15 min, 1000 cycles | Peel strength degradation $\leq$ roughened control | No degradation |
| Thermal Shock | Preconditioning (Level 3)<br>Reflow: 260$^{o}$C 3 times<br>TS (condition C): -65$^{o}$C to 150$^{o}$C, dwell 5 min, 1000 cycles (in liquid) | Peel strength degradation $\leq$ roughened control | 4% degradation vs. 8% for roughened control |
| THS | 85$^{o}$C, 85%RH – 1000hr | Peel strength degradation $\leq$ roughened control | 9% degradation - same as control |

# Plating: Enabling Fine-line patterning

ZETTACORE

| | L/S | Customer A | Customer B | Customer C | Customer D |
|---|---|---|---|---|---|
| Current capability | 50/50um | Pass | Pass | N/A | N/A |
| | 30/30um | Pass | Pass | N/A | N/A |
| | 20/20um | Pass | Pass | Pass | N/A |
| | 18/18um | Pass | Pass | Pass | N/A |
| Enabled capability | 14/14um | Pass | Pass | Pass | N/A |
| | 12/12um | Pass | TBD* | Pass | N/A |
| | 10/10um | Pass | TBD* | Pass | Pass |
| | 8/8um | Pass | TBD* | TBD* | Pass |

*** Requires etch / process modification**

## Patterned structures

Patterning completed on ZettaCore processed substrates to L/S of 8um

***Confirms value of ZettaCore technology in enabling advanced geometries***

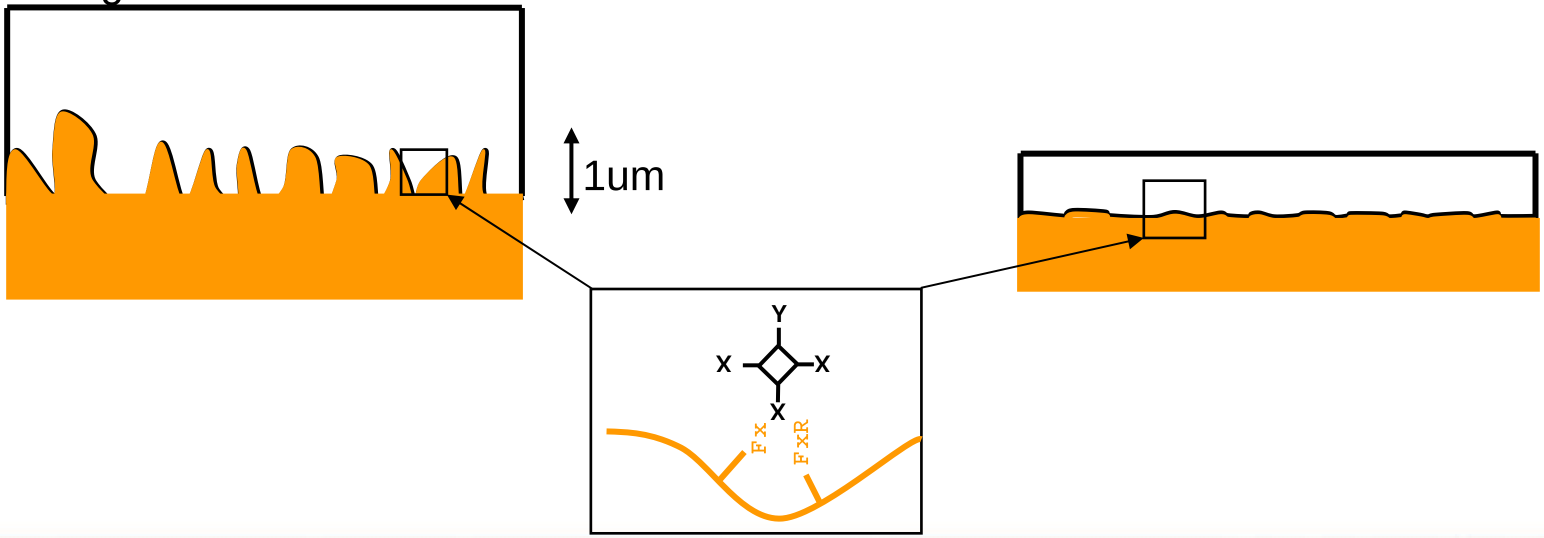
# Adhesion Issues in Lamination on Copper

- Fine line patterning (~10 um) requires smooth Cu surface
  - Mechanical adhesion insufficient for reliability of fine line traces
  - Conventional Cu roughening processes provide insufficient adhesion

- Adhesion mechanism for fine lines will depend on mechanical and chemical forces

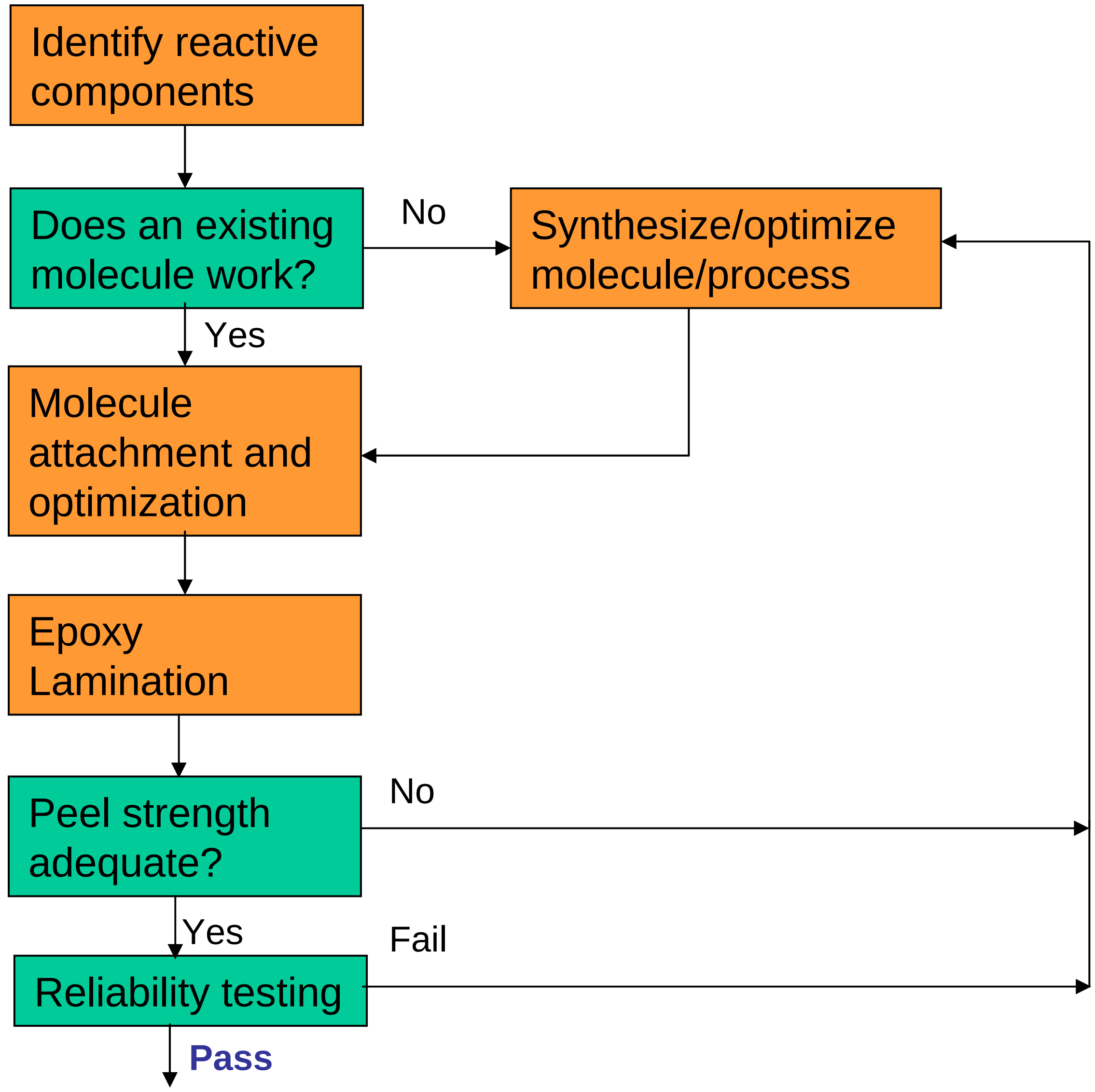
**Existing Approach** **New approach**

Roughened Cu surface “Smooth” Cu surface



# Optimization of Molecule Properties for Adhesion in Cu Lamination Process

ZETTACORE



# ZettaCore MI Process for Cu Lamination

ZETTACORE

**Molecule Attachment**

Surface Cleaning → Surface Conditioning → Surface Treatment → Baking Drying

**Lamination**

## Standard Chemistries/Processes

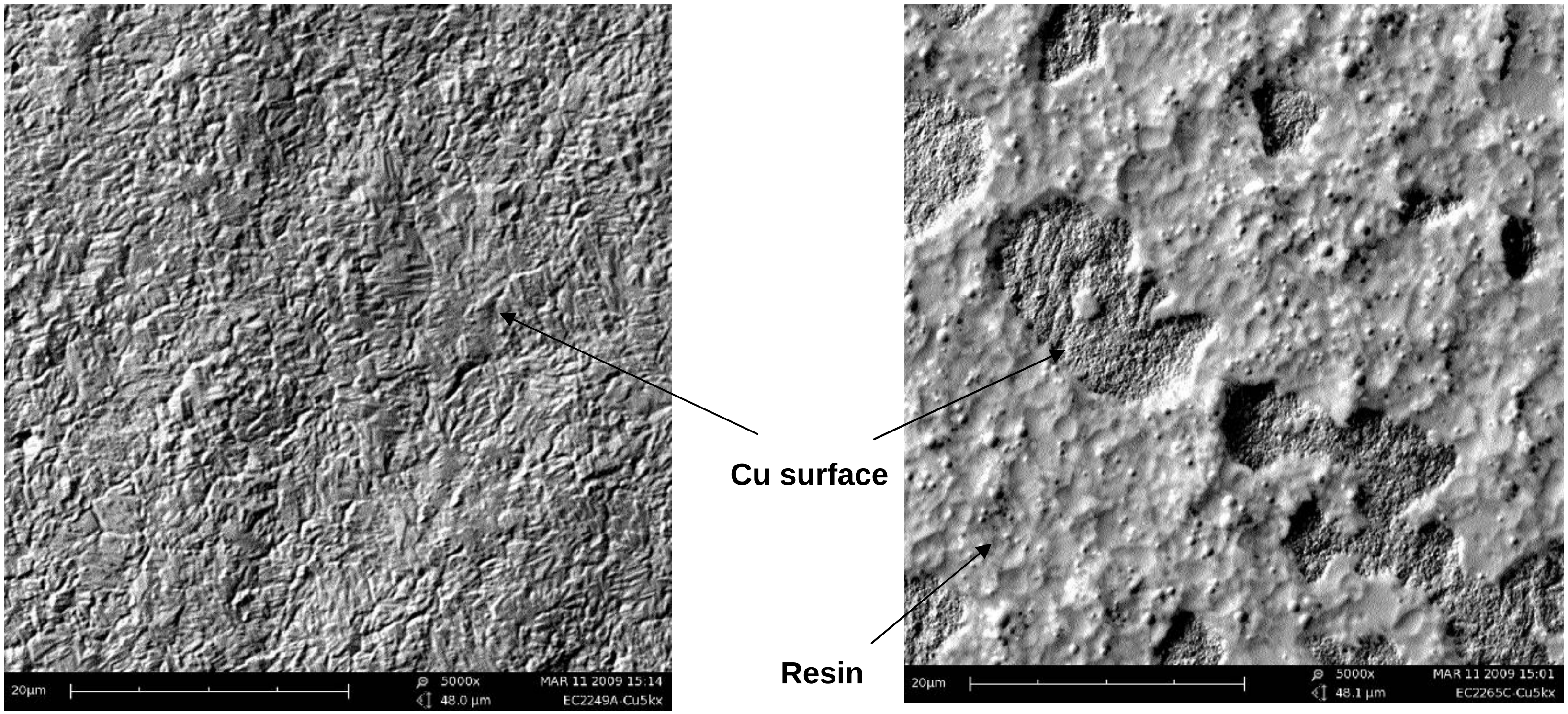
No need for changes in standard processes!!!

**Testing**

Peel Test → HAST → Repeat Peel Test

# SEM of Smooth and MI™–treated Copper Surfaces

## After HAST and Peel-back of laminated Epoxy

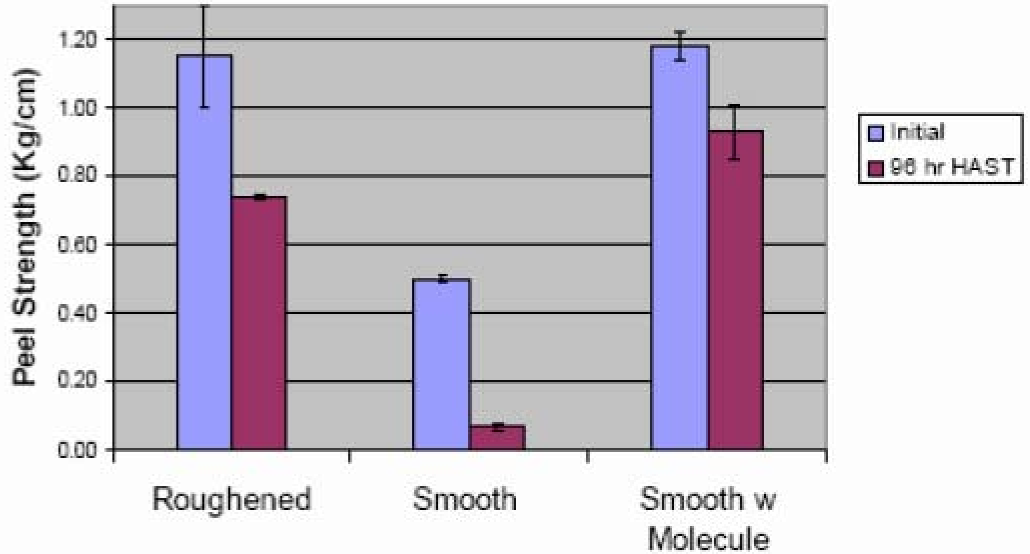



**Untreated Smooth Cu** | **Mi™ - Treated Cu Surface**

**Surface is clean Cu suggesting that the peeled surface breaks at the Cu-resin interface.**

**Most areas covered by resin suggesting Cu-resin interface breaks within the resin, not at the Cu-resin interface**

# Lamination: Peel Strength Data




| Substrates | Peel Strength (Kg/cm) | | Roughness ($R_a$, µm) |
|---|---|---|---|
| | Initial | 96 hr HAST | |
| Roughened | 1.15 | 0.74 | 0.53 |
| Smooth | 0.50 | 0.07 | 0.13 |
| Smooth w molecule | 1.18 | 0.93 | 0.13 |

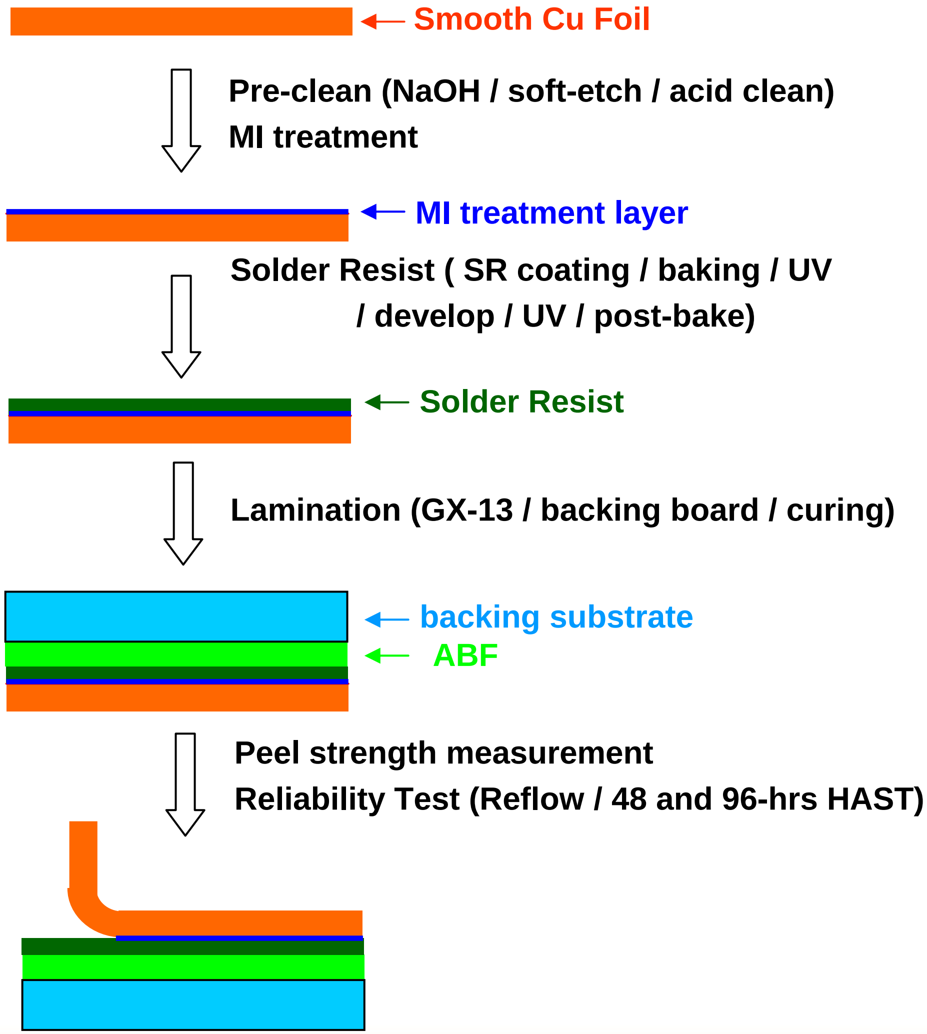
*Desired combination*

***ZettaCore treatment shows superior HAST stability – 21% degradation vs. 36% for roughened control***

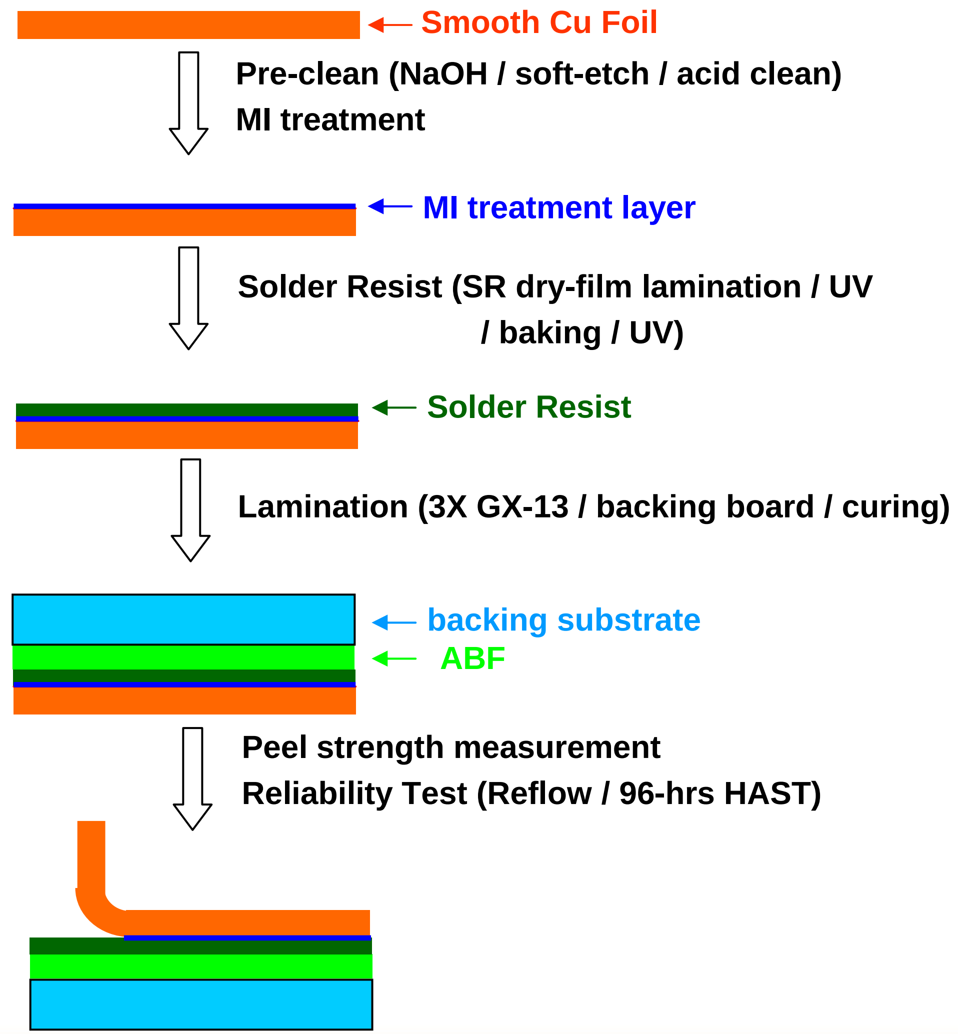
# Solder Resist: Paste and Dry Film Processes

ZETTACORE

## Paste SR Process

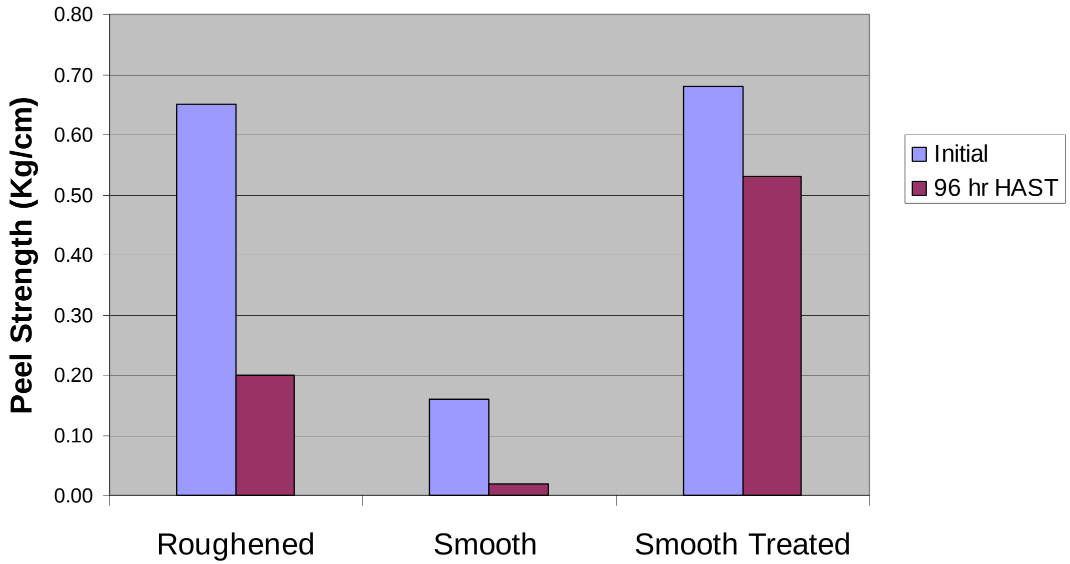



## Dry Film Resist Process



# Solder Resist: DFR Material Summary

ZETTACORE




| Substrates | Peel Strength (Kg/cm) | | Roughness ($R_a$, μm) |
|---|---|---|---|
| | Initial | 96 hr HAST | |
| Roughened | 0.65 | 0.20 | 0.53 |
| Smooth | 0.16 | 0.02 | 0.13 |
| Smooth w molecule | 0.68 | 0.53 | 0.14 |

***ZettaCore treated smooth Cu shows superior HAST stability and No undercut or delamination after subsequent processing (soft-etch and Ni/Au plating)***

# Lamination: Results Summary

ZETTACORE

Peel strength and HAST stability:

- 1.33 Kg/cm before and 1.15 Kg/cm after HAST
- 14% degradation vs. 36% for roughened control

Lamination and HAST stability on patterned Cu lines:

- ZettaCore process does not roughen the Cu lines
- No delamination after HAST
- Isolation resistance > $10^{12}\ \Omega$ after HAST

Laser drilling and via clean/plating compatibility:

- No delamination or undercut post via-clean and plating

***ZettaCore process enhances adhesion without roughening the Cu surface***
***Demonstrated through HAST testing***

# MI Results Summary

- ZettaCore solutions available for all 3 interfaces
    - e-less plating on smooth dielectric
    - resin lamination on smooth copper
    - solder resist on smooth copper
- Provides finer line dimensions and improved reliability performance