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Stress in Electroless Copper Films: Analysis by *in situ* X-Ray Diffraction and Curvature Methods

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Stress in Electroless Copper Films: Why bother?

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Stress in Electroless Copper Films

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Why bother?

- **Copper deposit stress has a major influence on**
  - the deposit's blistering behavior
  - and hence on its adhesion to the substrate
  - and hence on the quality of its performance
- **Substrate materials for advanced applications**
  - Low roughness (build-up film laminates for semi-additive process (SAP) and trench-filling technologies, glass substrates for display applications)
  - Challenging for copper film adhesion
  - Bending can also be an issue (wafers)
- **Meeting the adhesion requirements of such materials**
  - Adapted surface treatments (conditioners, non-etching adhesion promotion (NEAP))
  - Electroless copper deposits with suitable characteristics

Copper deposit stress affects adhesion

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Stress in Electroless Copper Films: What does it look like?

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Stress in Electroless Copper Films

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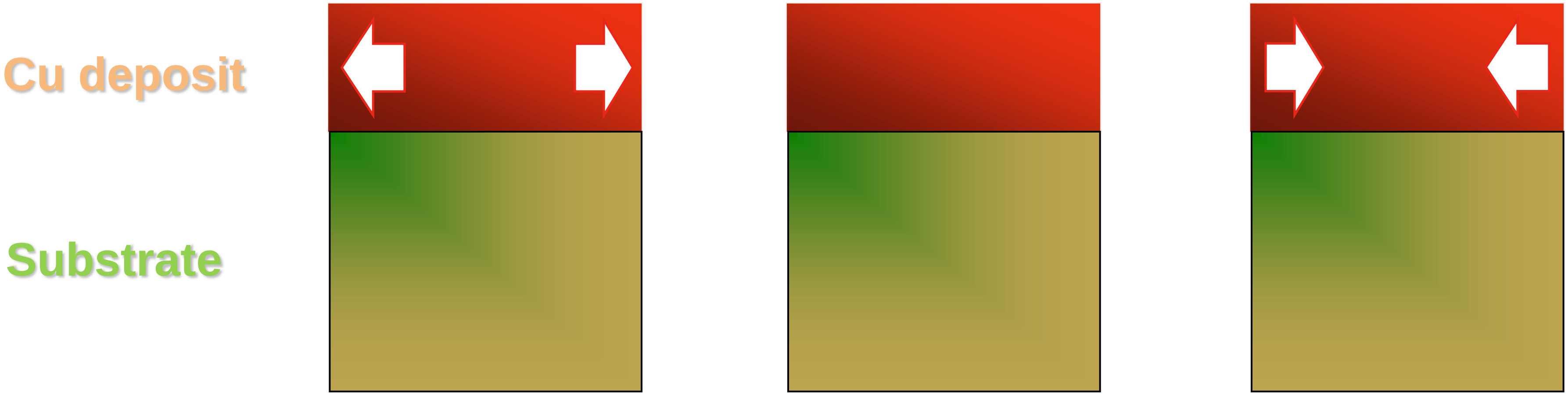
What does it look like?

tensile stress
$\sigma > 0.0$ kg/mm^2

relaxed
$\sigma = 0.0$ kg/mm^2

compressive stress
$\sigma < 0.0$ kg/mm^2



Tensile stress:

- In-plane lattice constant is larger than out-of-plane lattice constant
- **Blistering tendency is low**
- Cracking tendency can be high

Relaxed:

- Lattice constants are equivalent to those of the ideal face-centred-cubic (fcc) crystal structure of copper
- **No cracks or blisters occur**

Compressive stress:

- In-plane lattice constant is smaller than out-of-plane lattice constant
- **Blistering tendency is high**
- Cracking tendency is low

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Stress in Electroless Copper Films: How is it measured?

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Deposit Stress Analyzer (DSA)

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Stress in Electroless Copper Films

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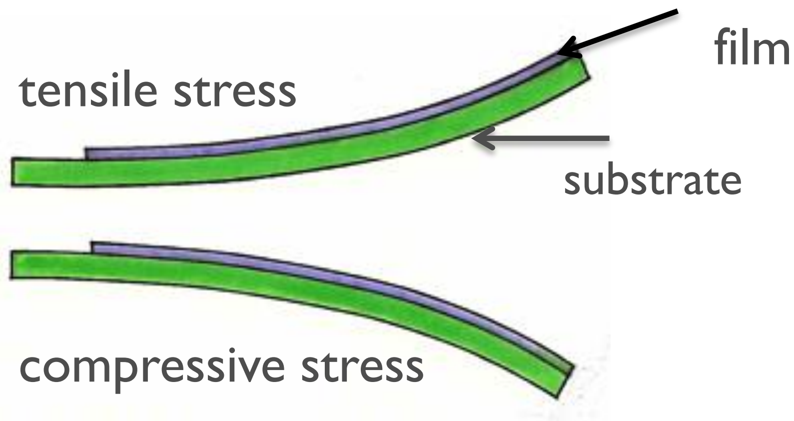
Measurement by DSA



Stress, $\sigma = (2fC)/(3t)$

$2f$ → distance between strip ends on scale
C → supplier's calibration constant
t → coating thickness

A new frontier for deposit stress measurements, Frank H. Leaman, Specialty testing and Development Company Inc., PA USA.

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Stress in Electroless Copper Films

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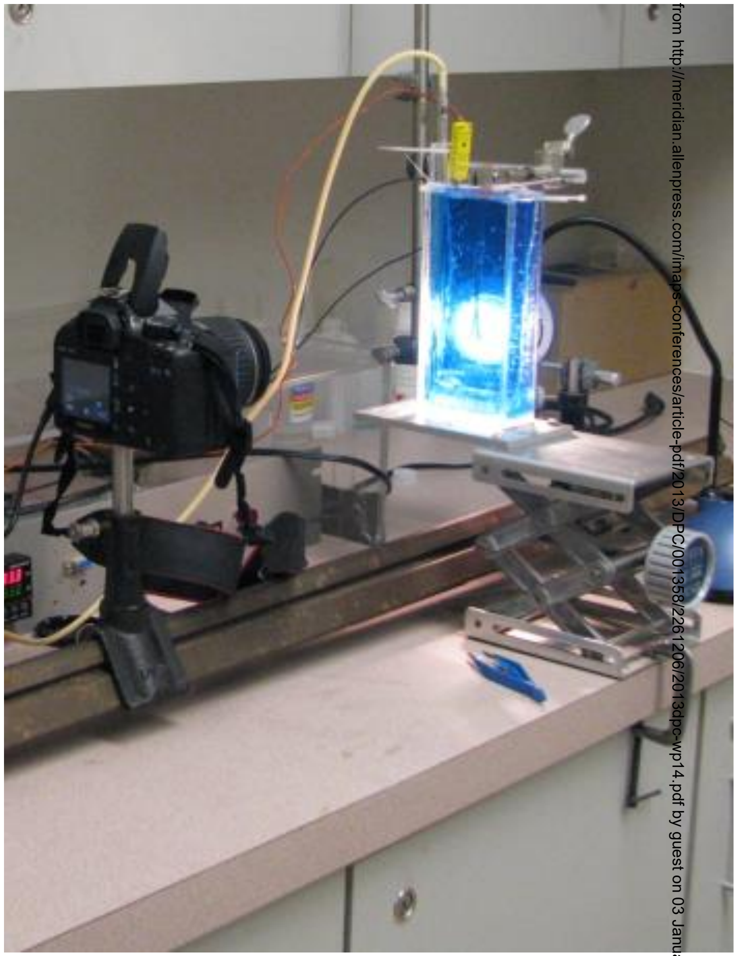
Measurement by DSA

- **Established method for thick and thin electrodeposited films**
- **Advantages**
  - *In situ* method
  - Easy to use
  - Low cost (< $300)
  - High resolution (0.01 GPa (= 1 kg mm^{-2})), even for thin films
  - Straightforward theoretical derivation
- **Disadvantage**
  - Bronze or copper substrate → representative of printed circuit board (PCB) substrates?



Is DSA suitable for electroless copper deposits?

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Spiral Contractometer (SC)

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Stress in Electroless Copper Films

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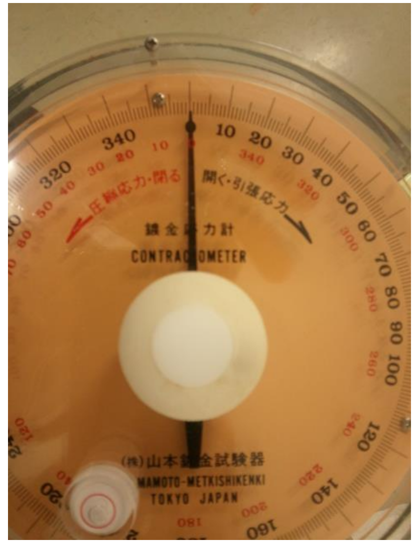
Measurement by SC



Stress (corrected), $\sigma_{corr} = \sigma[1+(E_{coat}d)/(E_{subs}t)]$

$\sigma = Z\alpha_{meas}/t$ $\qquad$ $Z = (2m_{cal}gr)/(pd\alpha_{cal})$

σ → uncorrected stress
E → Young's modulus
t → coating thickness
α_{meas} → deflection angle
m_{cal} → calibration mass

g → gravitational constant
r → lever arm
p → pitch of helix
d → thickness of helix strip
α_{cal} → deflection angle

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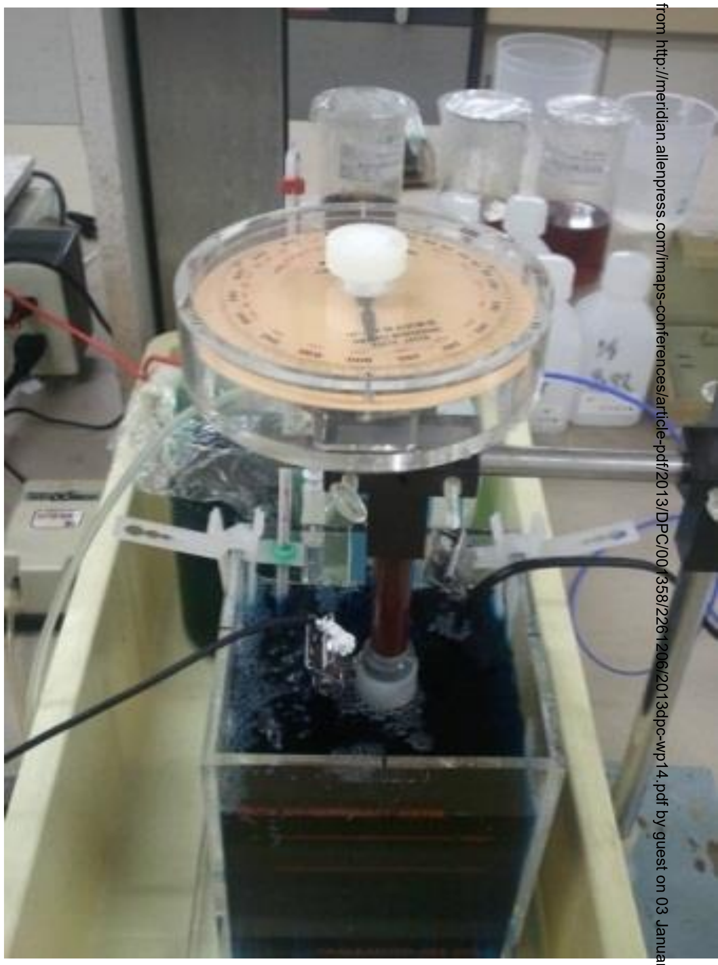
Stress in Electroless Copper Films

Measurement by SC

- **Established method for thick electrodeposited films**
- **Advantages**
  - *In situ* method
  - Straightforward theoretical derivation
- **Disadvantages**
  - Setting up the measurement is more time consuming than DSA
  - Low resolution and reproducibility for near-zero stress values (sub-µm-thick films (6 kg mm^{-2}))
  - Moderate cost (~ $3000)
  - Stainless steel substrate → current required to initiate deposition. Realistic of electroless copper?
  - Stainless steel substrate → representative of PCB substrates?



Is SC suitable for electroless copper deposits?

X-Ray Diffraction (XRD)

Stress in Electroless Copper Films

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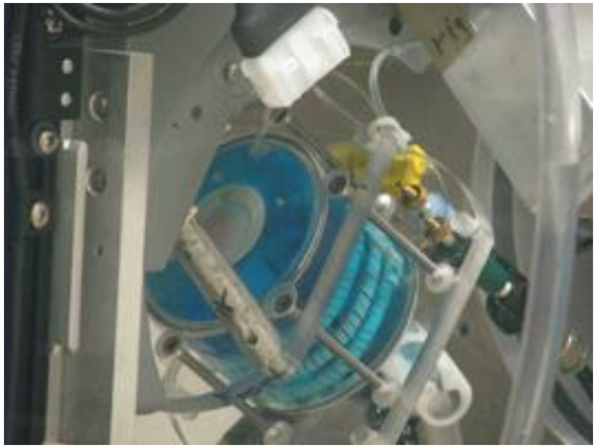
Measurement by XRD



- The measurement cell is tilted back and forth between two angles (ψ = 0° and 65°)
- At ψ = 0°, out-of-plane ($a_\perp$) lattice constant observed
- At ψ = 65°, projected in-plane ($a_\parallel$) lattice constant observed
- $a_\perp > a_\parallel \rightarrow$ compressive strain
- $a_\perp < a_\parallel \rightarrow$ tensile strain
- $a_\perp = a_\parallel \rightarrow$ strain-free

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Stress in Electroless Copper Films

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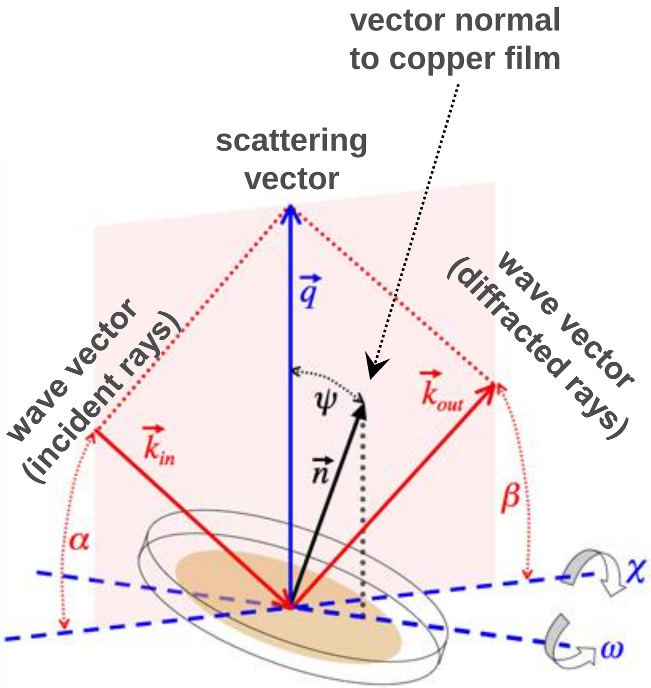
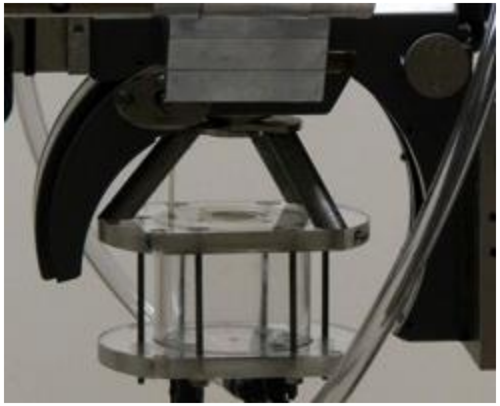
Measurement by XRD

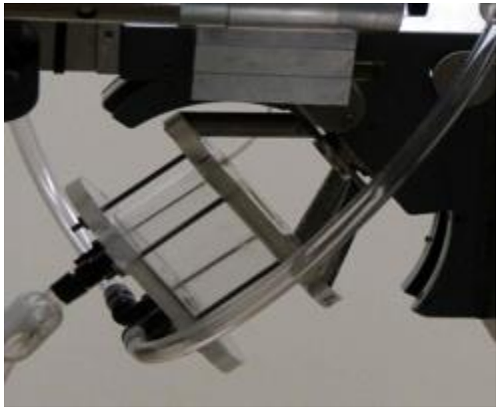


α = angle of incidence of X-rays with respect to copper film
β = angle of diffracted X-rays with respect to copper film

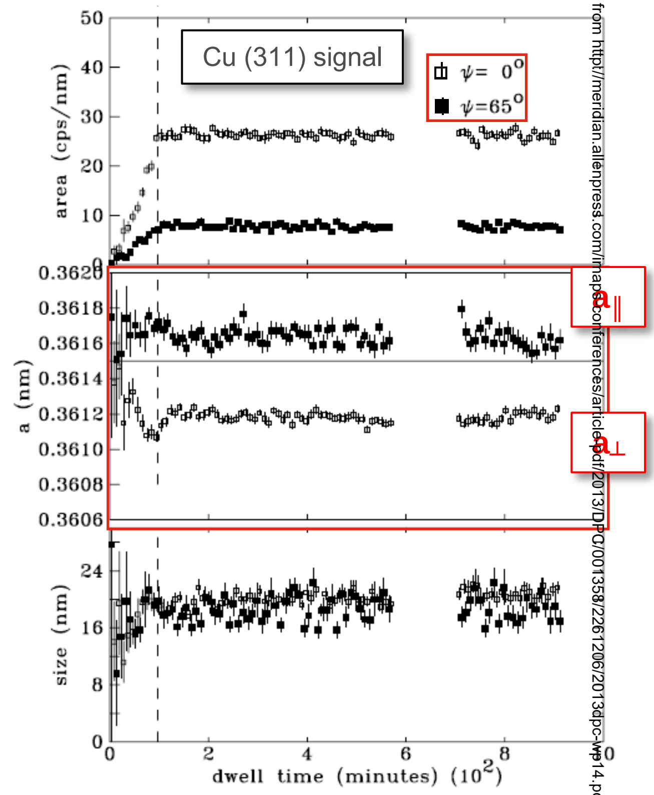
The angle ψ between the scattering and copper film normal vectors depends on the angles χ and ω



Cell at $\psi = 0°$



Cell at $\psi = 65°$



Stress, $\sigma_\parallel = [(a_\parallel - a_\perp)E]/[a(1+\nu)]$
For copper, $E/(1+\nu) = 73.8$ GPa

$E \rightarrow$ Young's modulus of copper
$a \rightarrow$ lattice constant of fcc copper
$\nu \rightarrow$ Poisson's ratio

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Stress in Electroless Copper Films

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Measurement by XRD

- **Advantages**
  - *In situ* method
  - Direct measurement of strain in macroscopically ordered copper crystals
  - Good resolution (2 kg mm^{-2}), even for thin films
  - Measurement on acrylonitrile butadiene styrene (ABS) substrate → plastic more representative of PCB substrates

- **Disadvantages**
  - Very high equipment cost (> $100000)
  - Highly qualified staff required for operation
  - Time-consuming
  - Not practicable in industrial plating tank

Is XRD the method of choice for electroless copper deposits?

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Stress in Electroless Copper Films: Comparison of DSA, SC and XRD

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Stress in Electroless Copper Films

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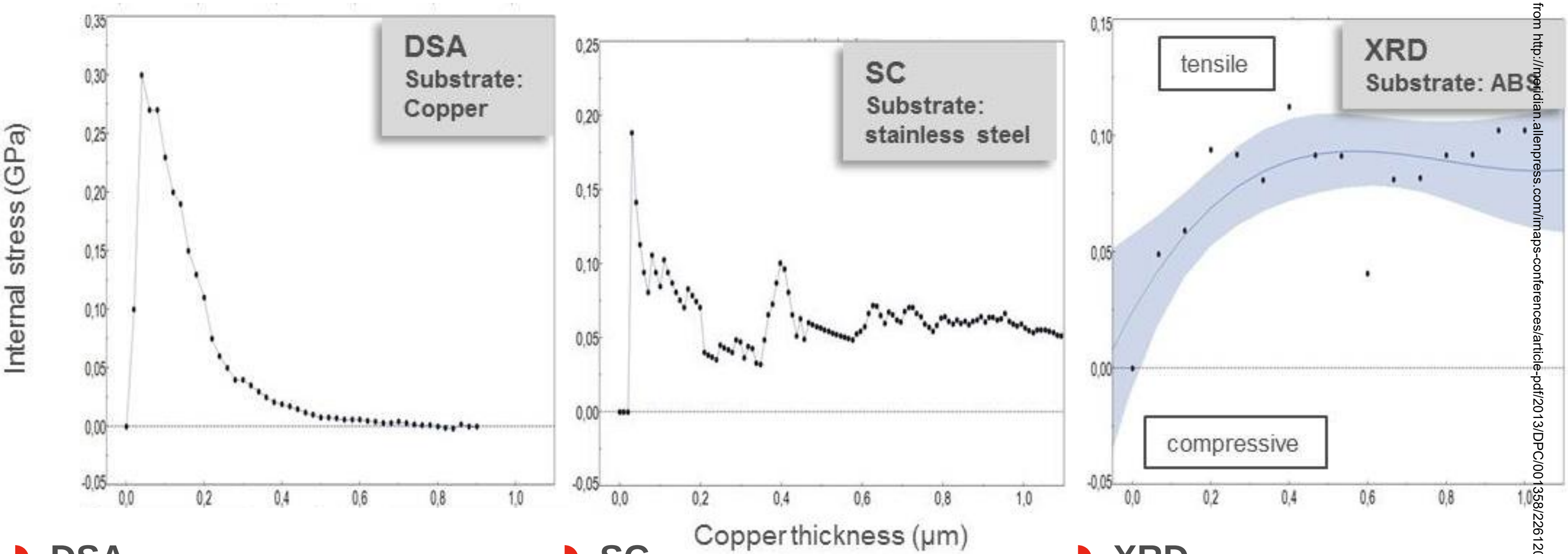
Comparison of DSA, SC and XRD



DSA

- High tensile stress (0.3 GPa) at thickness, *d* < 0.1 µm
- Stress-free at *d* > 0.5 µm
- 1/*d*-like relaxation, but the tensile stress rises to 0.09 GPa during the following 8 hours after deposition

SC

- Qualitatively similar to DSA
- Higher tensile stress of 0.05 GPa at *d* > 0.5 µm

XRD

- Linear increase of tensile stress up to 0.3 µm
- Constant tensile stress of about 0.09 GPa at *d* > 0.3 µm, even more than 8 hours after deposition

TOTAL

Stress in Electroless Copper Films

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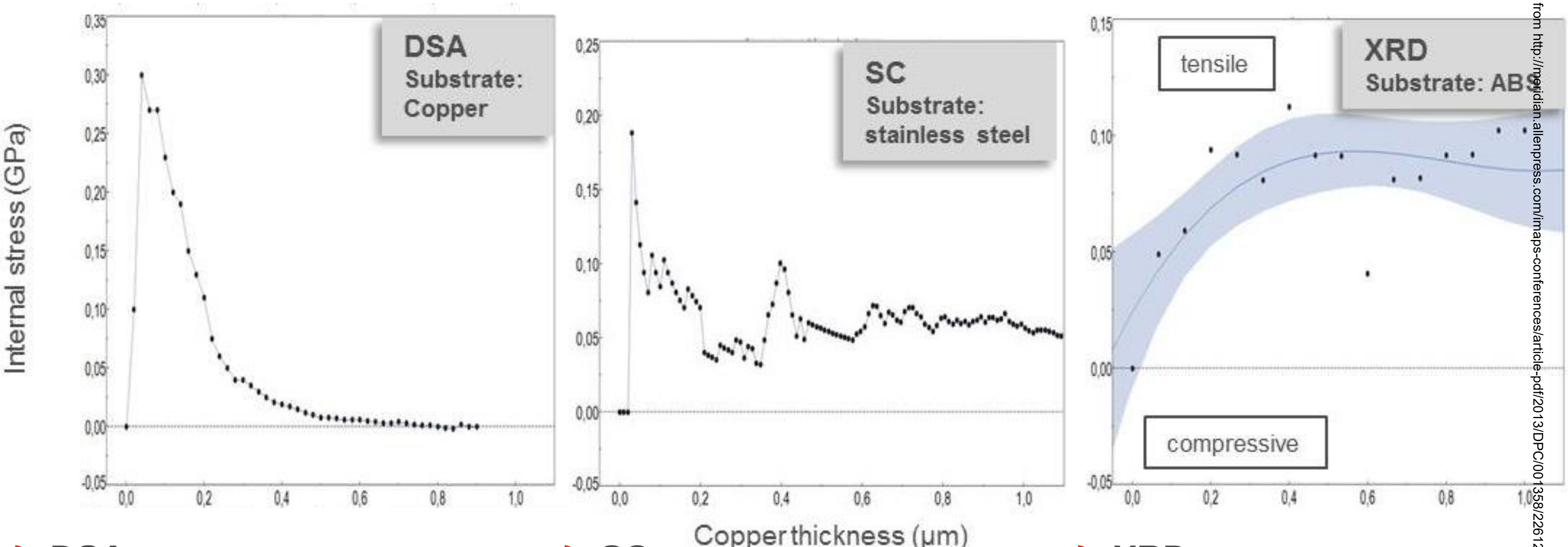
Comparison of DSA, SC and XRD



- **DSA**
  - High tensile stress (0.3 GPa) at thickness, *d* < 0.1 µm
  - Stress-free at *d* > 0.5 µm
  - 1/*d*-like relaxation, but the tensile stress rises to 0.09 GPa during the following 8 hours after deposition
- **SC**
  - Qualitatively similar to DSA
  - Higher tensile stress of 0.05 GPa at *d* > 0.5 µm
- **XRD**
  - Linear increase of tensile stress up to 0.3 µm
  - Constant tensile stress of about 0.09 GPa at *d* > 0.3 µm, even more than 8 hours after deposition

3 different methods,

3 different substrates,

3 different results!

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Stress in Electroless Copper Films: How to control it?

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Stress in Electroless Copper Films

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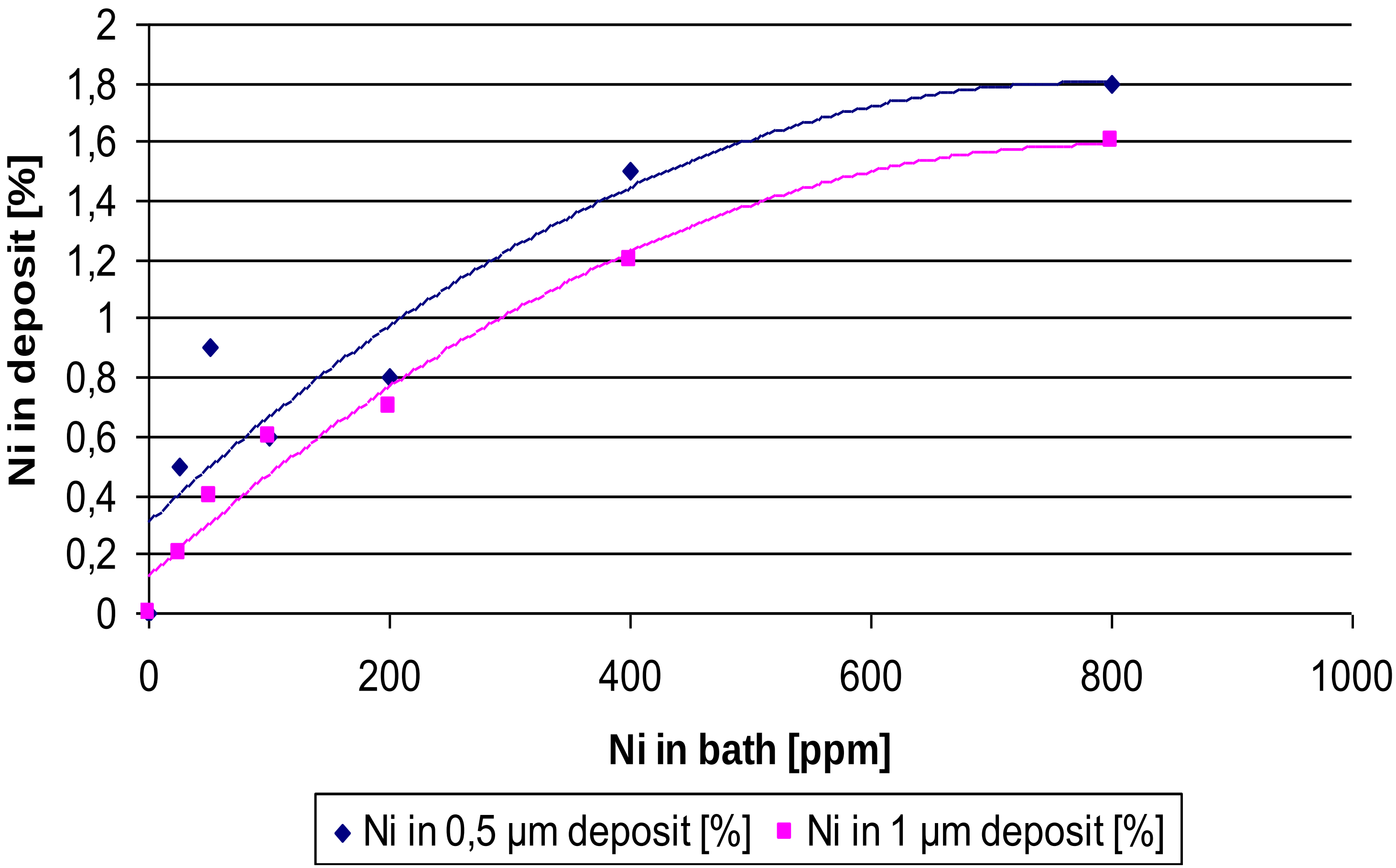
How to control it? One way is to vary the nickel content in the bath…



High nickel in bath, high tensile stress in deposit, even though deposit only contains about 1% nickel!

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Stress in Electroless Copper Films

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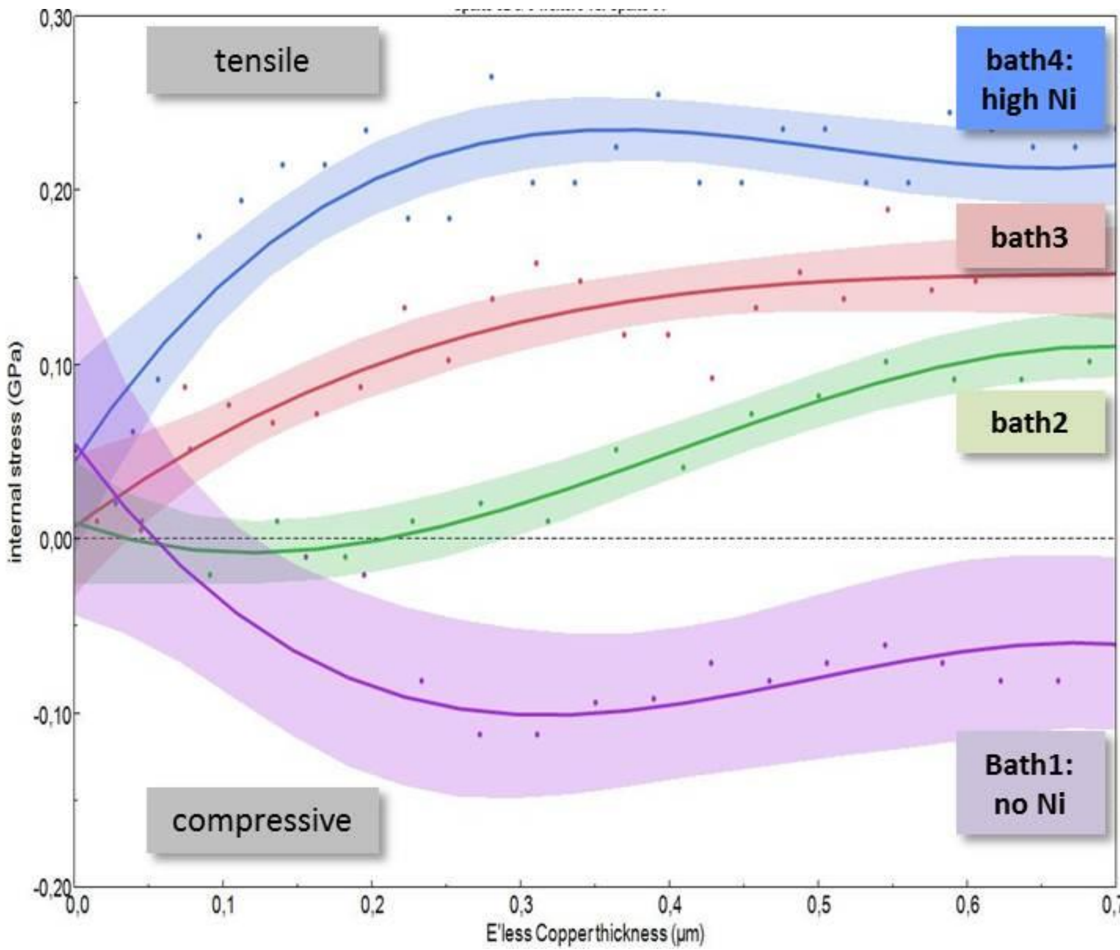
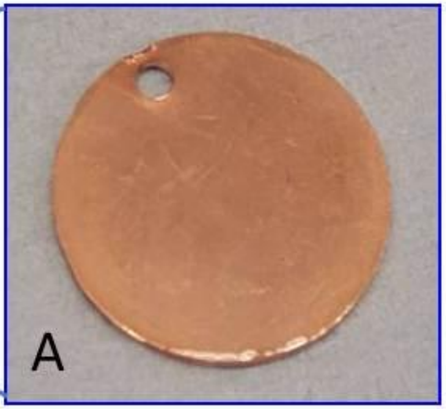
How to control it? One way is to vary the nickel content in the bath…





Less nickel, less tensile, less adhesion!

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Stress in Electroless Copper Films: Is the substrate important?

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Stress in Electroless Copper Films

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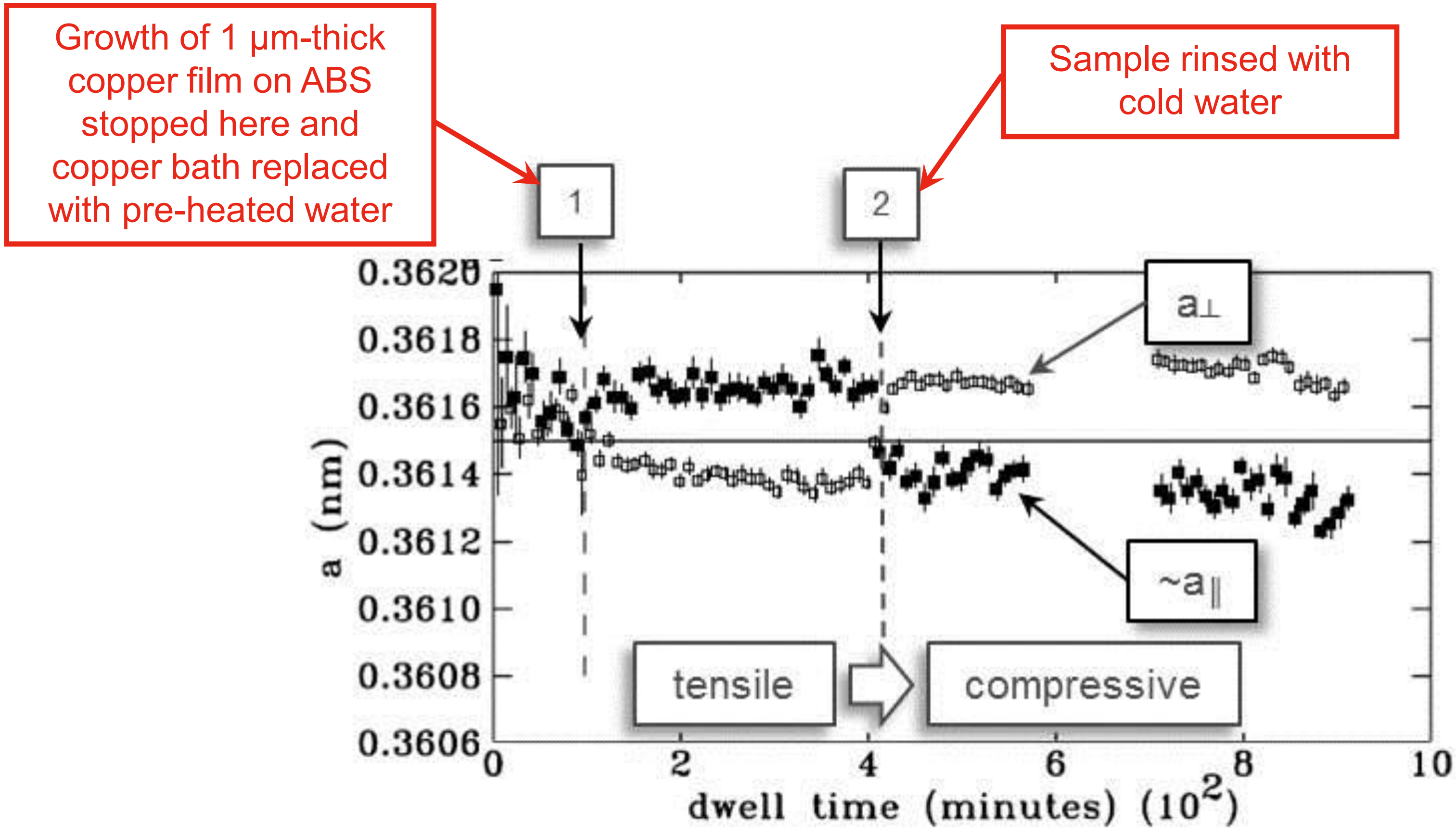
Is the substrate important?



- **Quantitative stress investigations of electroless copper for PCBs**
  - should utilise PCB-comparable substrates
  - should account for the coefficient of thermal expansion (CTE) of the substrate

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Stress in Electroless Copper Films

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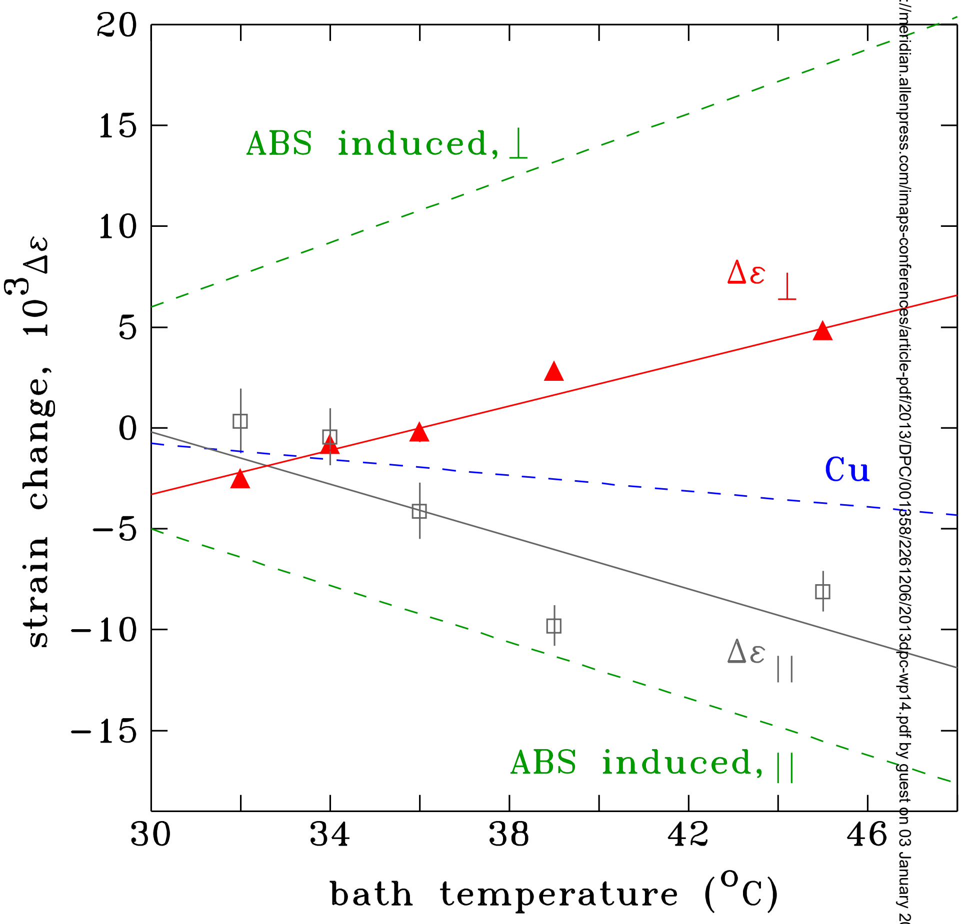
A more detailed analysis of stress changes during cooling

- **Strain change**
  - **In-plane:** $\Delta\varepsilon_{\parallel} = \Delta a_{\parallel}/\langle a\rangle$
  - **Out-of-plane:** $\Delta\varepsilon_{\perp} = \Delta a_{\perp}/\langle a\rangle$
- **For each data point, $\Delta a_{\parallel}$ and $\Delta a_{\perp}$ evaluated based on XRD data immediately prior to and immediately after cooling from bath to rinse-water temperature (22 °C)**
- **Data points show development of compressive stress on cooling**
  - **Contraction in film plane**
  - **Expansion in perpendicular direction**



Compressive stress develops on cooling!

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Stress in Electroless Copper Films

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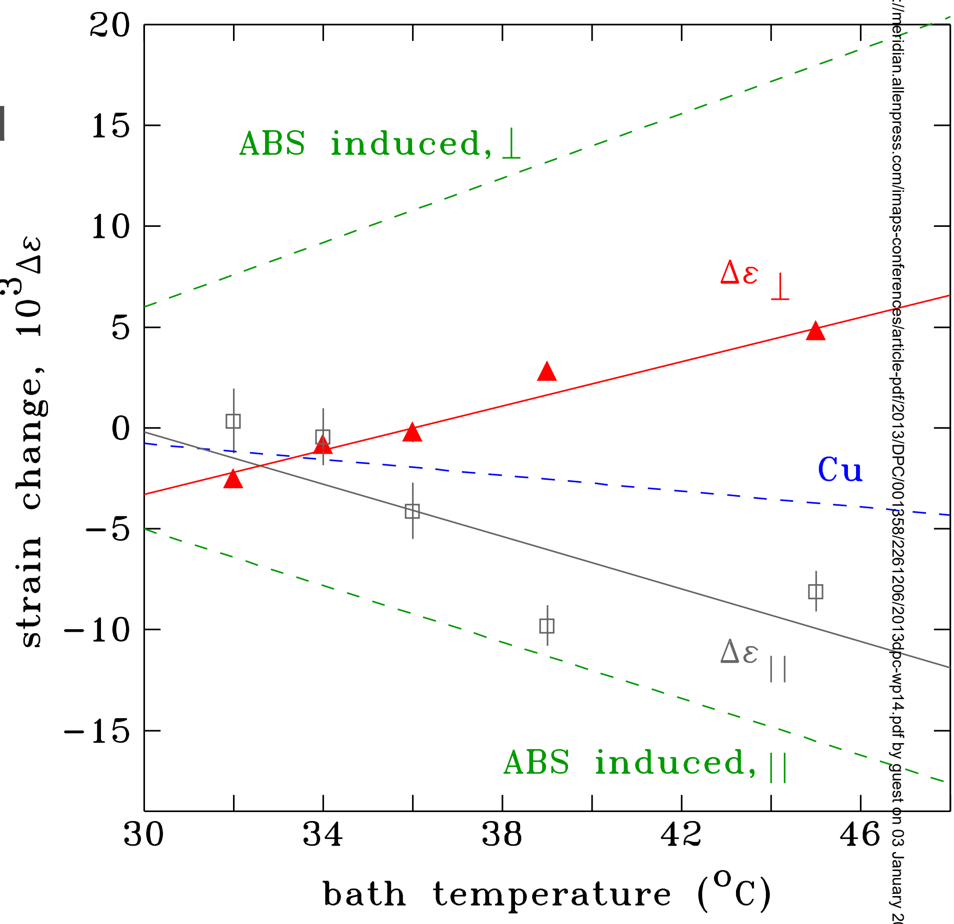
A more detailed analysis of stress changes during cooling

- **Limiting case 1: film complies with thermal contraction of copper (dashed blue line)**
  - **Film contracts independently of substrate**
  - **$\Delta\varepsilon_{\parallel} = \Delta\varepsilon_{\perp} = \alpha_{Cu}\Delta T$ (α_{Cu} = CTE of copper)**
- **Limiting case 2: film complies with thermal contraction of the ABS substrate within and perpendicular to the film plane (dashed green lines)**
  - **$\Delta\varepsilon_{\parallel} = \alpha_{ABS}\Delta T$ (α_{ABS} = CTE of ABS)**
  - **$\Delta\varepsilon_{\perp} = -(2v\Delta\varepsilon_{\parallel})/(1 - v)$**



Effect of substrate on thin copper films cannot be ignored!

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Stress in Electroless Copper Films: Conclusions and Summary

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Stress in Electroless Copper Films

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Conclusions and Summary

- Comparison of methods
  - **DSA →** Low-cost, high-resolution, easy-to-use method, but…

    …substrate (bronze or copper) is not representative of PCB substrates!
  - **SC →** Moderate-cost, low-resolution method utilising stainless steel substrate.

    Substrate not representative of PCB substrates, method not suited for thin deposits and application of current to initiate deposition is necessary! → Least recommendable method!
  - **XRD →** Despite high cost of method and high operator skill required…

    …high-resolution method utilising PCB-comparable substrates, suitable for thin deposits. → Most recommendable method for thin deposits (<2 µm), such as electroless copper films!

XRD → Most suited method for thin deposits!

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Stress in Electroless Copper Films

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Conclusions and Summary

- Stress and its implications
  - Tensile stress helps avoid blistering
  - Nickel promotes formation of tensile-stressed deposits
  - Substrate CTE must be taken into account
  - Pre-stressed deposits rather than stress-free deposits might be better

Stress-free is not always best!

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Contributors

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