# Whisker/Hillock Formation on As-electrodeposited and Indentation Stressed Sn Film

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# Background: Pb-free Solder and Pb-free Surface Finishes for Electronics

***Experimental and Thermodynamic Assessment of Sn-Ag-Cu Solder Alloys***

Journal of Electronic Materials, Vol. 29, No. 10 (2000) pp. 1122-1136

***The effect of Pb Contamination on the Solidification Behavior of Sn-Bi solders***

Journal of Electronic Materials, Vol. 30, No. 1 (2001) pp. 45-52

# Questions

- From where does Sn come to form whiskers?
- How do the Sn whisker nucleate and grow?
- How is the compressive stress developed?
- What is the intrinsic stress of Sn deposit?
- What is the critical stress level to grow whiskers?
- Is there any substitute for Pb?
- Is there any difference in microstructure between Sn and Sn-Pb deposit?
- Are there any correlations between Sn whisker formation and
  - Microstructure and/or crystallographic,
  - Sn oxide surface film, and
  - IMC formed at the interface?

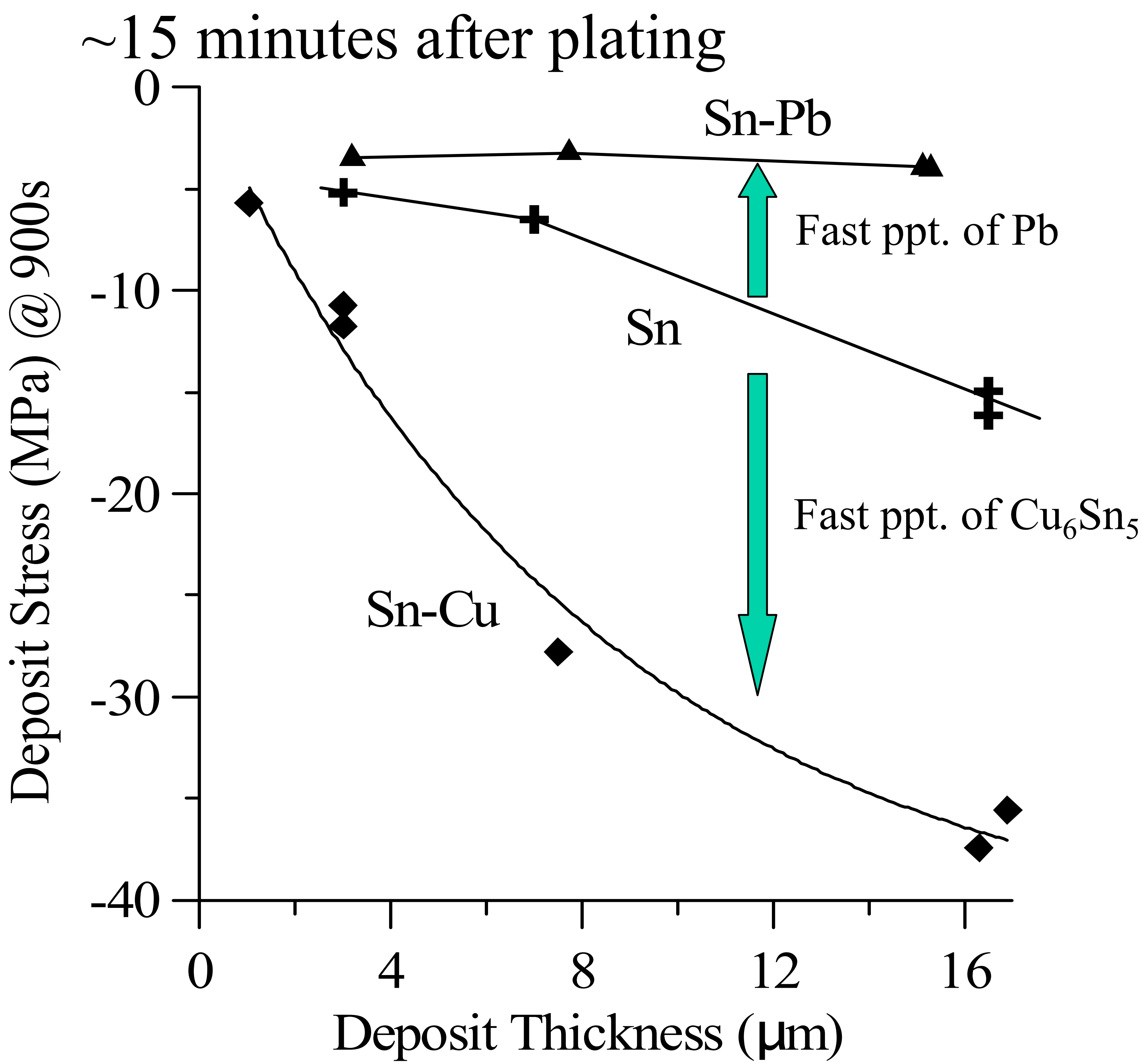
# Suggested Sn Whisker Growth Mechanism:

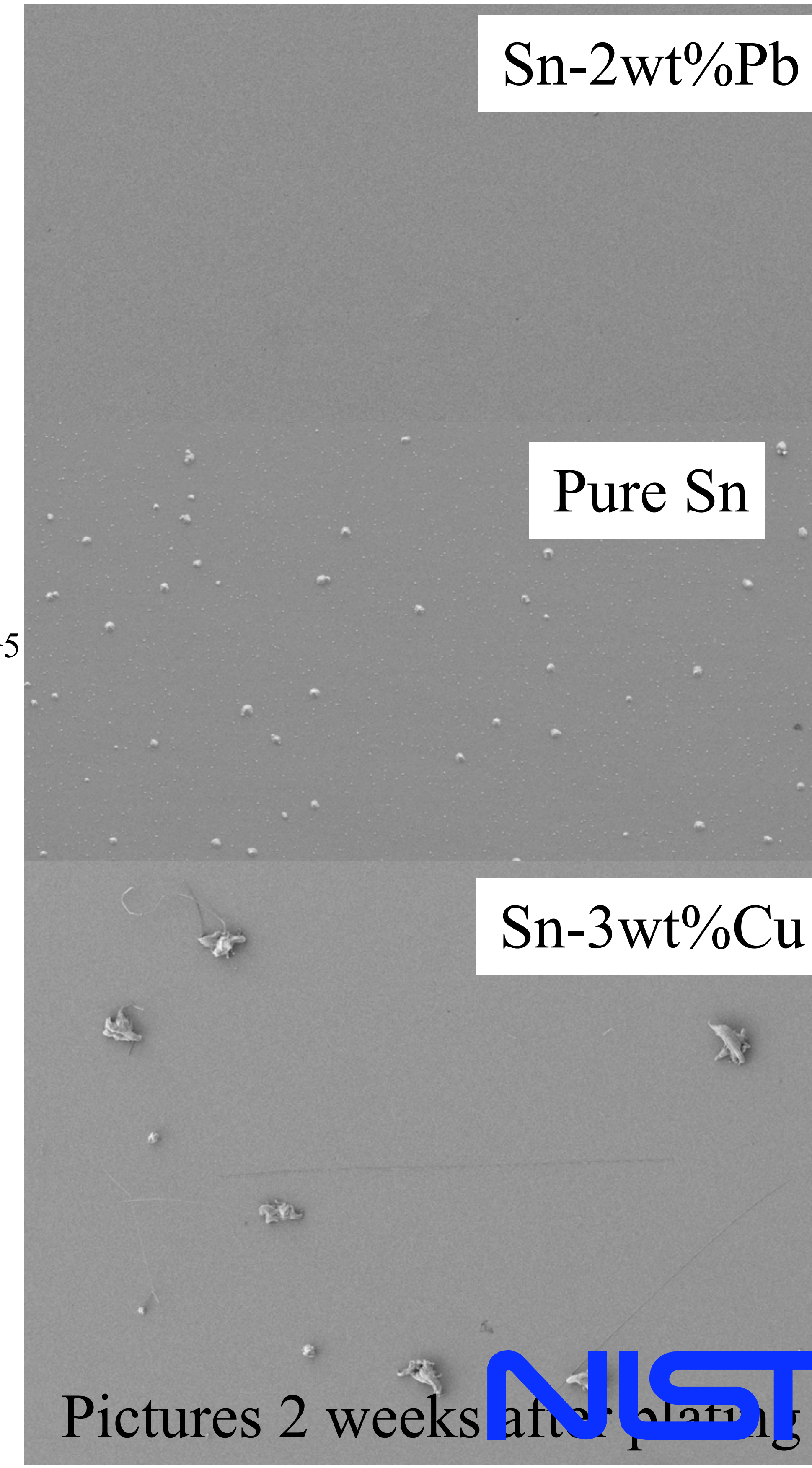
## Acta Materialia, Vol. 53 (2005) pp. 5033-5050

- Sn and Sn-Cu microstructure showed columnar grain structure and hillocks and whiskers observed, respectively
- Sn-Pb microstructure showed equiaxed grain structure and no whisker observed
- Only the Sn-Cu deposit showed $Cu_6Sn_5$ IMC at the grain boundary
- No preferred growth orientation of hillocks on the Sn deposit
- From cantilever beam tests:
  - bright Sn, Sn-Cu, and Sn-Pb deposits showed the compressive stress initially
  - they released their stress levels
  - and then a further compressive stress was built by the IMC growth at the interface
- Suggested Sn hillock/whisker growth mechanisms:
  - ✓ the difference of initial stress came from supersaturation of Cu or Pb in the electrolyte and from rapid precipitation process
  - ✓ the stress relief happened by a localized Nabarro-Herring-Coble creep
  - ✓ the grain boundary parallel to the surface promoted uniform expansion like Sn-Pb equiaxed grains
  - ✓ the IMC at the grain boundary pinned the grain boundary migration and formed whiskers

# Compressive Stress in Electrodeposits /Whisker Formation

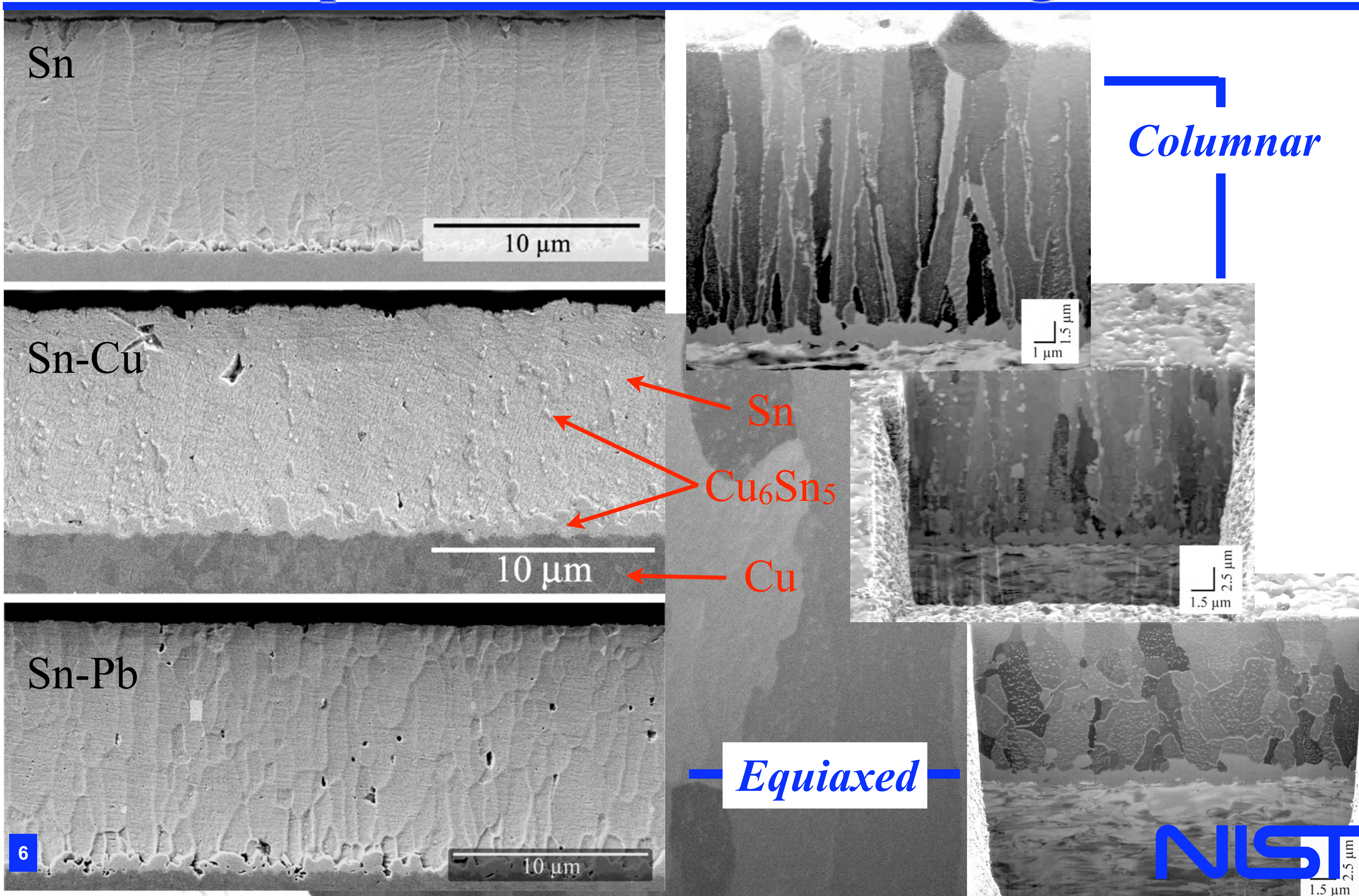
15 m thick



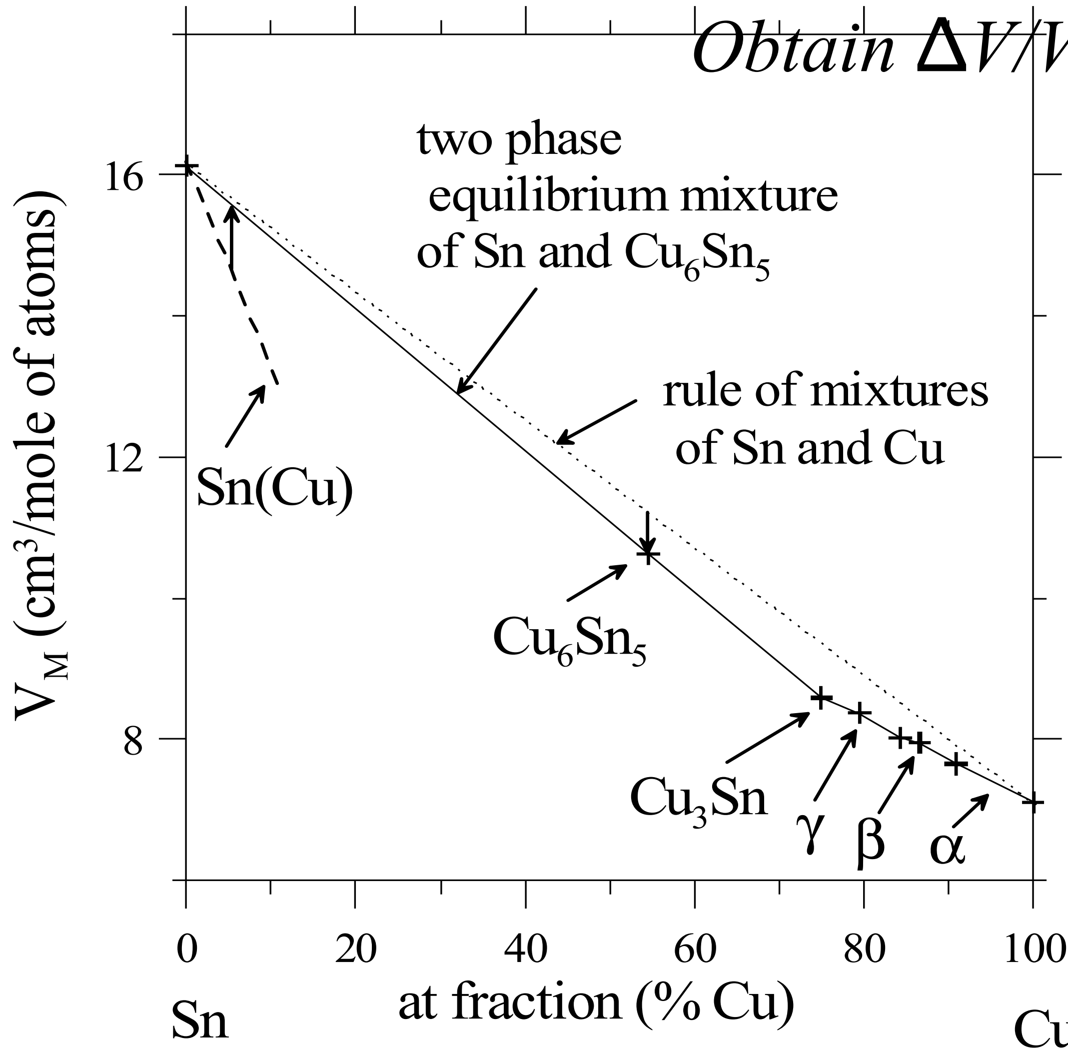

***Trend with thickness suggests a gradient of stress in the deposit.***

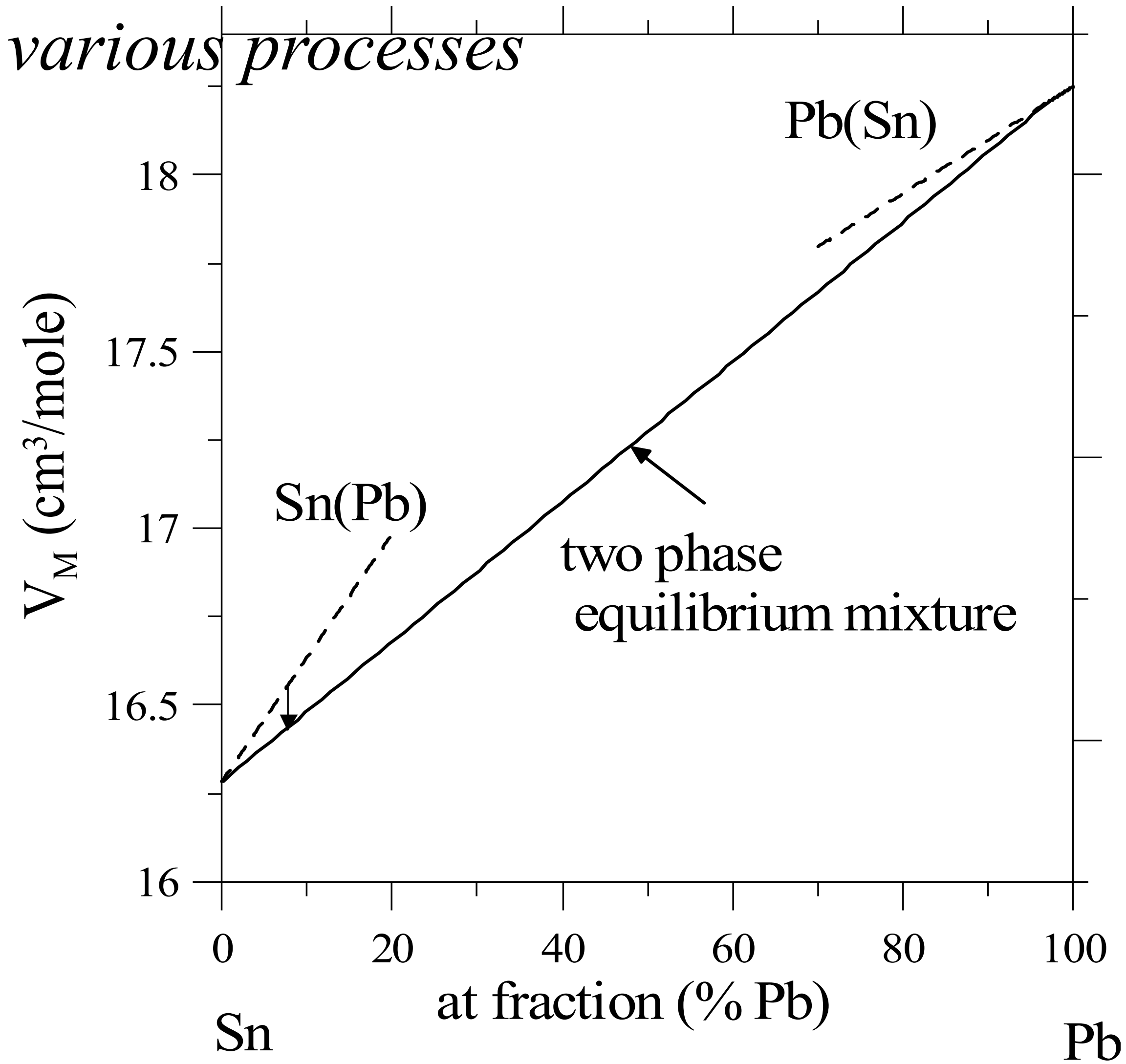
# Cross-sectional Microstructures of Sn, Sn-Cu, and Sn-Pb Deposits: Mechanical Polishing and FIB



# Sn-Cu and Sn-Pb Molar Volume vs. Composition

*Obtain ΔV/V for various processes*



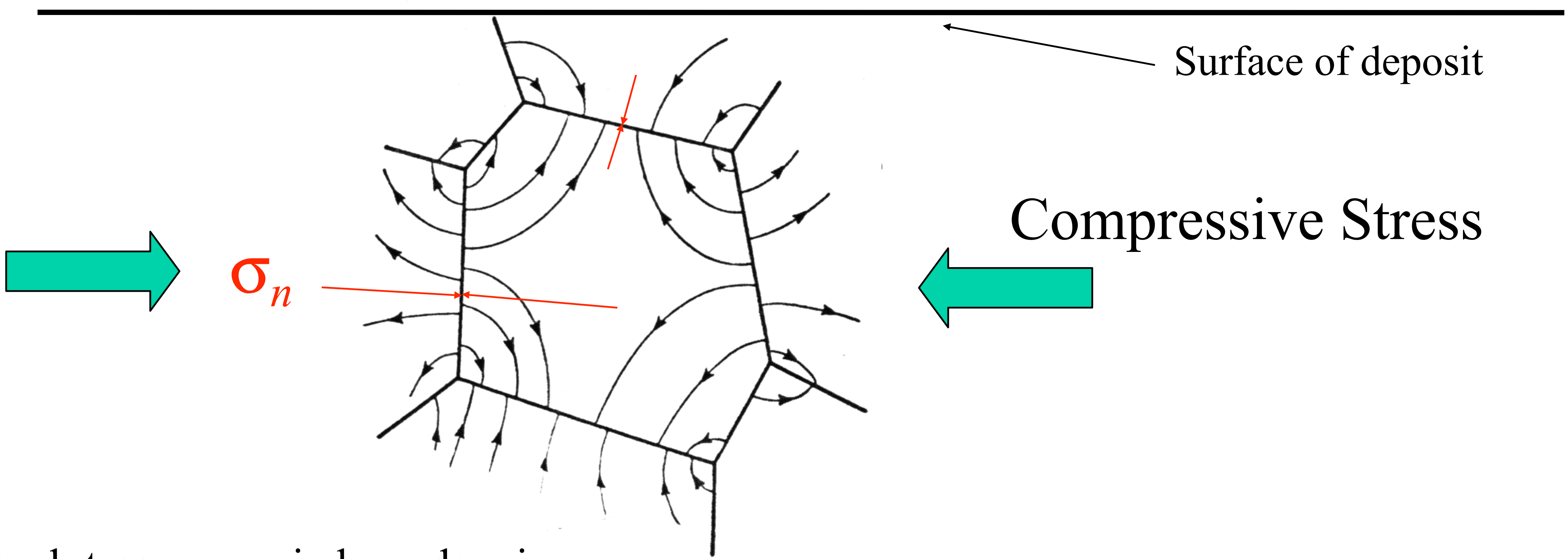

*Fast Processes*

- (Sn,Cu)→ Sn + $Cu_6Sn_5$ increases in molar volume
- (Sn,Pb)→ Sn + Pb decreases molar volume

- Sn + Cu → $Cu_6Sn_5$ decreases molar volume

*Slow Process*

# Diffusional Creep




Normal strees on grain boundary is

$$\sigma_n = \sigma_{ij} n_i n_j$$

Diffusion Potential is

$$M_{Sn-vacancy}\Big|_{gb\ w/normal\ \vec{n}} = -V_M \sigma_n$$

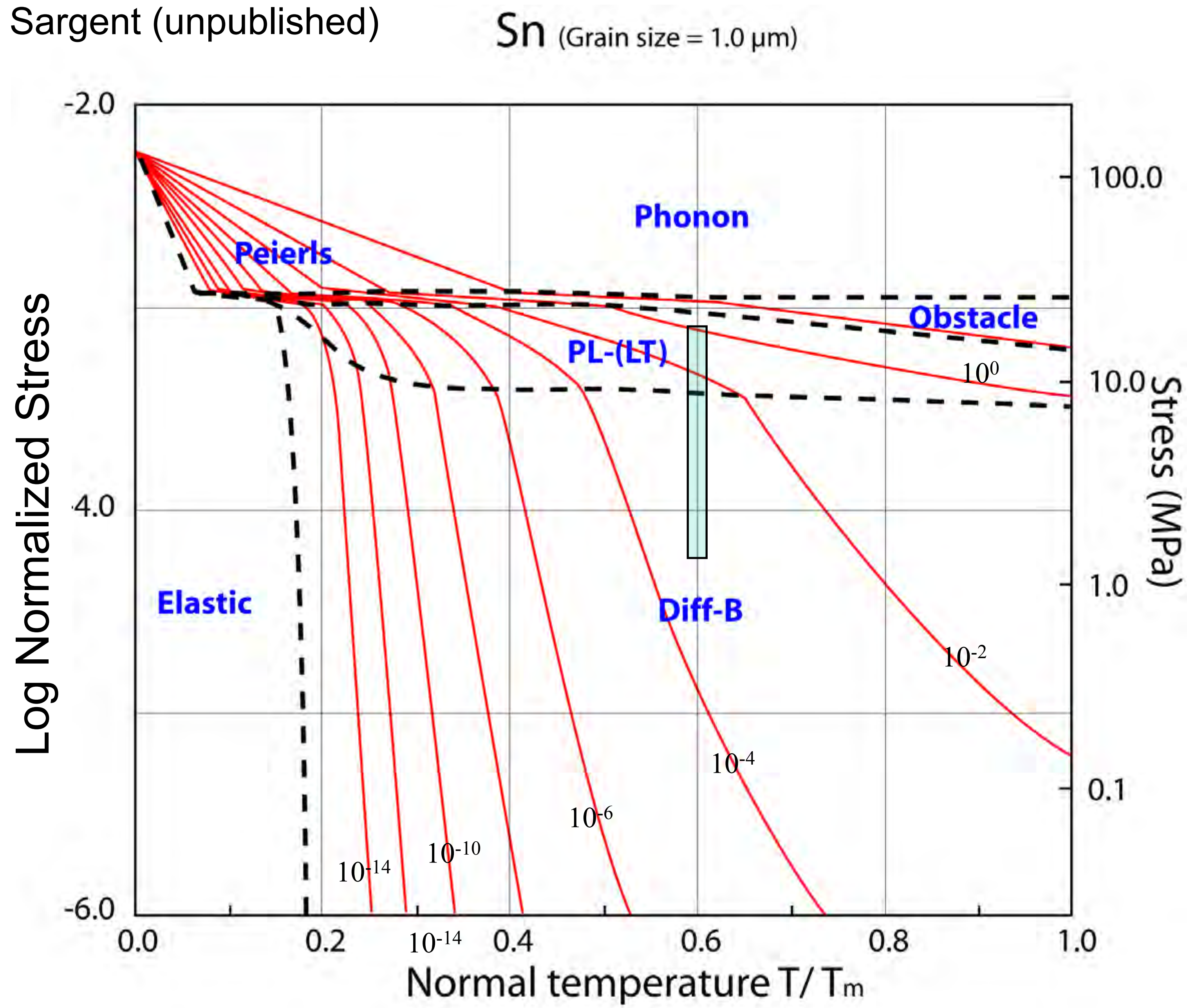
Flux due to gradient in diffusion potential

$$\vec{J}_{Sn} = -D \nabla M_{Sn\,v}$$

- Diffusion in bulk: Nabarro-Herring creep
- Diffusion on GB: Coble creep

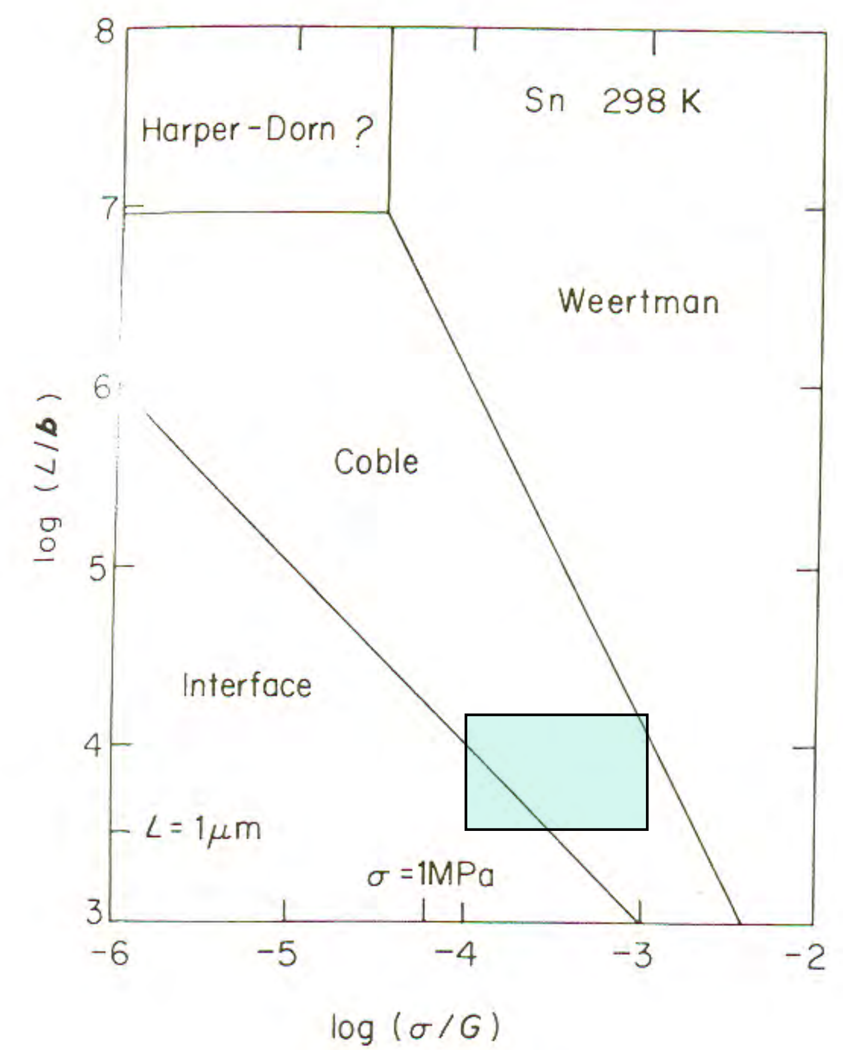
# Deformation Mechanism Maps: Coble Creep Expected

P.M. Sargent (unpublished)




NOTE Obstacle: Obstacle controlled slip (probably forest dislocations)
Peierls: Lattice resistance controlled slip
PL-(LT): Low temperature (dislocation core diffusion) power law creep
Diff-B: Diffusional flow by grain boundary diffusion

J.H. Schneibel & P.M. Hazzeldine (1983)

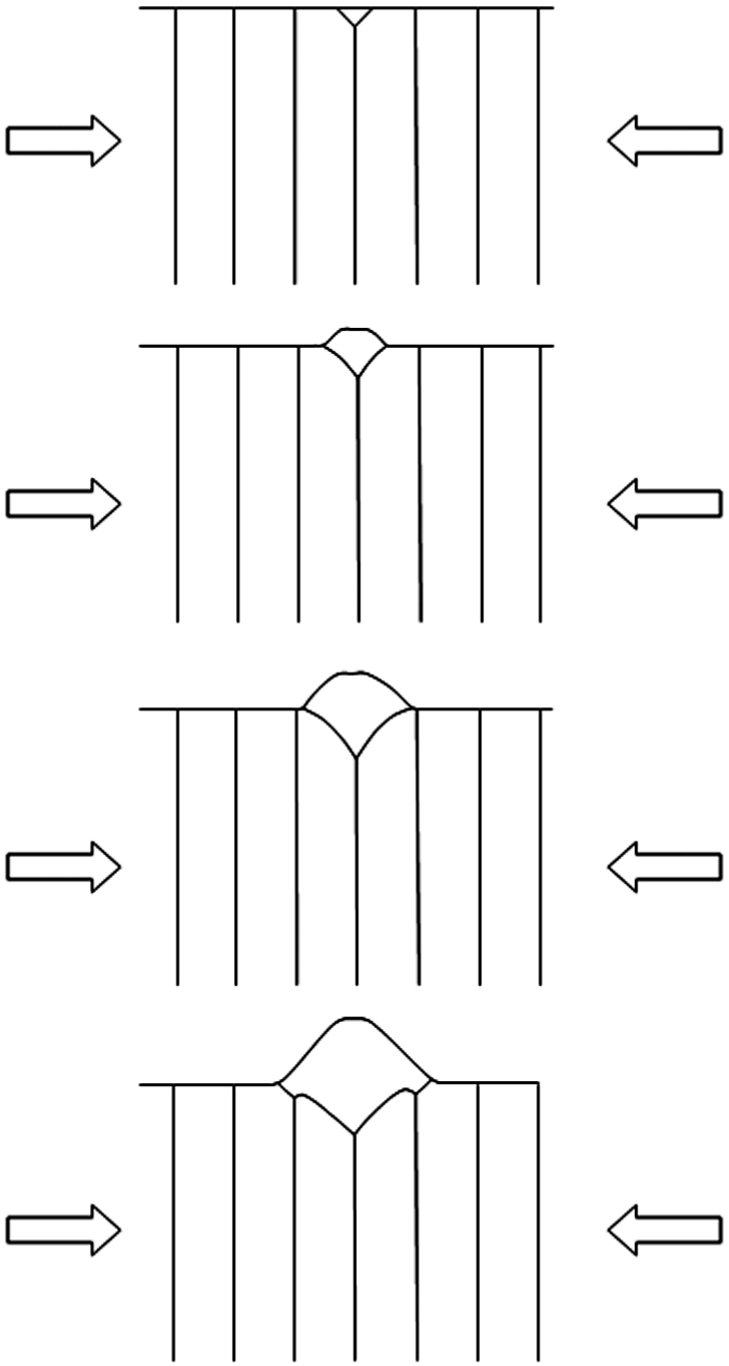



GB's have trouble emitting vacancies

0.6 $T/T_m$ of Cu = 542 ºC

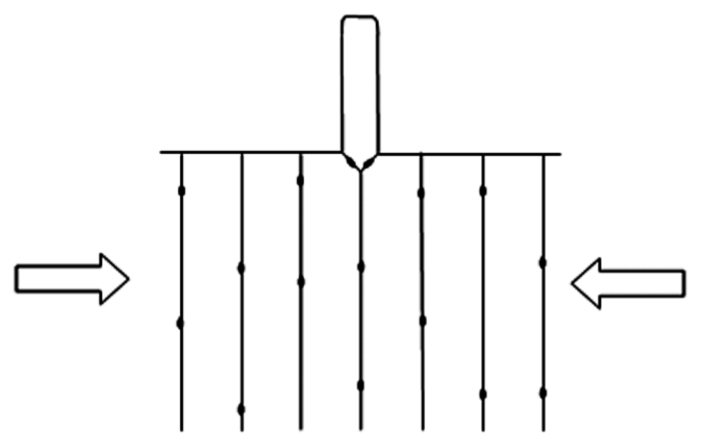
# Effect of Grain Shape and Mobility on Whisker & Hillock Formation

## Sn



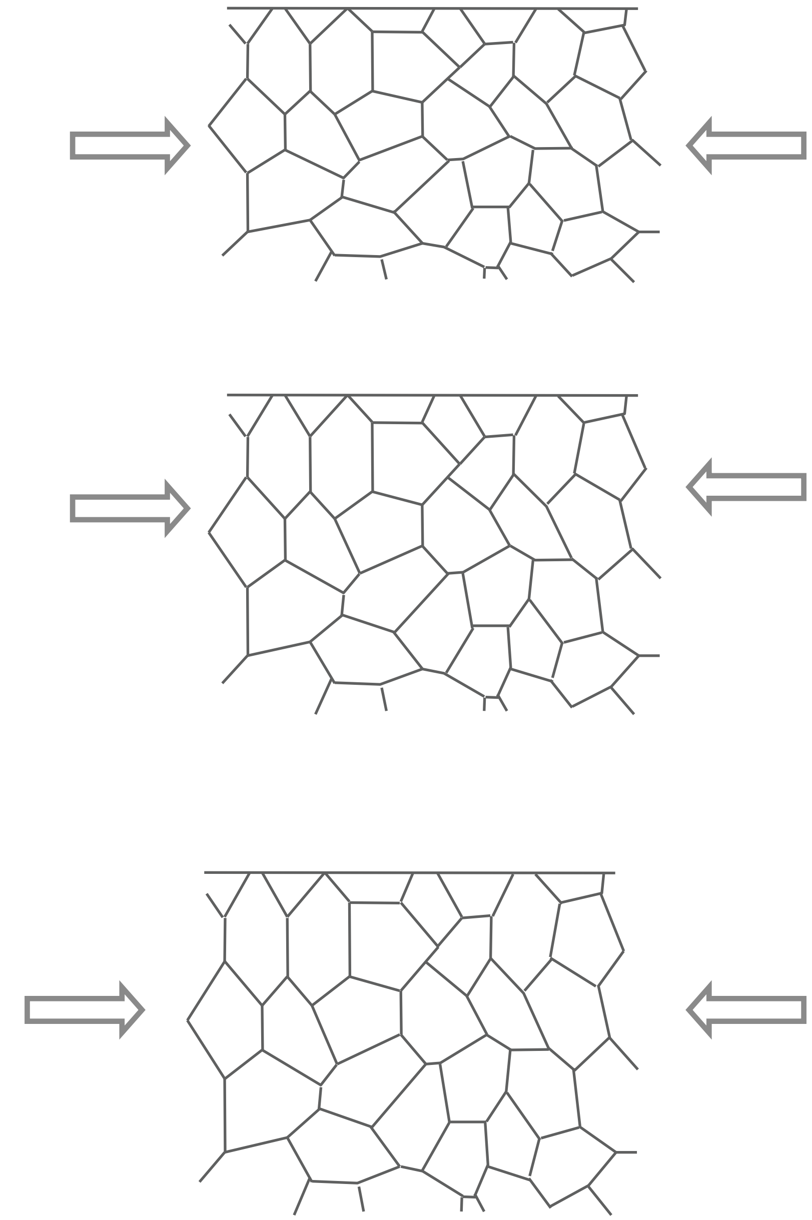
Columnar grain boundaries are mobile ⇒ hillocks

## Sn-Cu



Columnar grain boundaries are pinned ⇒ whiskers

## Sn-Pb



Equiaxed grain boundaries ⇒ general Coble creep



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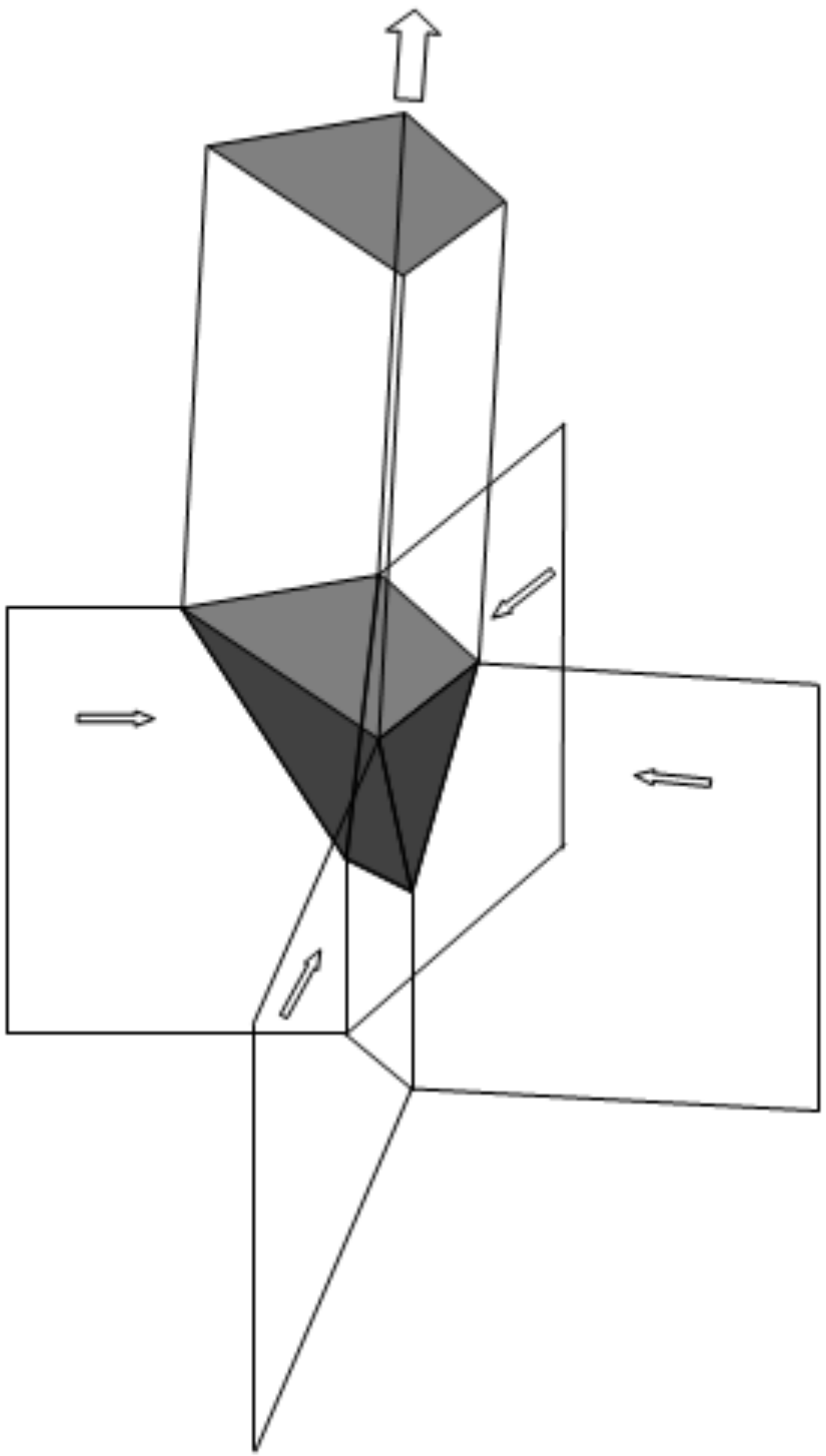
# Creep as a Mechanism of Whisker Formation



- Consideration of 3-D important
- Surface grain necessary in mostly columnar structure.
- Localized Nabarro-Herring-Coble creep
- Grain faces normal to stress has higher chemical potential than grain faces parallel to stress
- Grain boundary diffusion along grain faces from high to low chemical potential.
- Accretion of Sn on faces most parallel to stress
- Push up of “whisker grain”
- Curved whisker due to nonuniform accretion at base



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# Other Published Results in Sn Whiskers @ NIST

- Effects of Cu addition on Sn electrolytes
  - ✓ 50 ppm of Cu addition start to form whiskers
  - ✓ For the Sn-Cu deposit, IMC observed at the grain boundary
  - ✓ As Cu concentration increases, columnar grains become a smaller diameter
- Surface oxide effect on Sn whisker growth
  - ✓ After 9 days storage in 2 $x10^{-9}$ Pa, Sn whiskers were observed
- Sn-Cu on Tungsten
  - ✓ Sn whisker forms without the IMC at the interface
- Modification of Sn grain structure by pulse plating
  - ✓ Sn-Bi deposit showed the equiaxed structure by pulse plating but not for pure Sn
- Whisker/Hillock Formation Depending on the Current Density (in progress)



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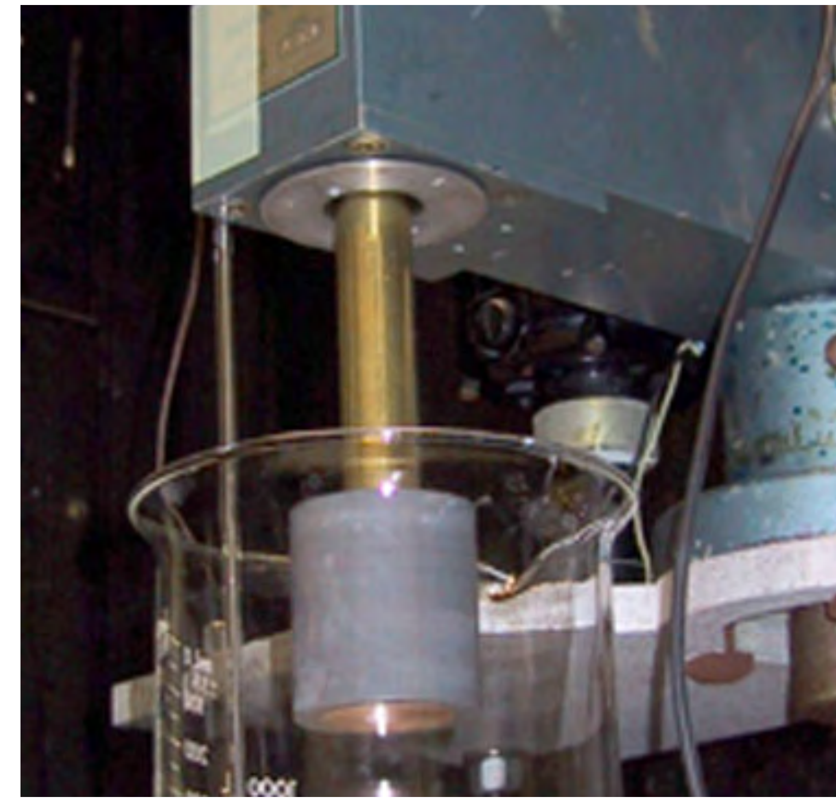
# Whisker/Hillock Formation Depending on the Current Density

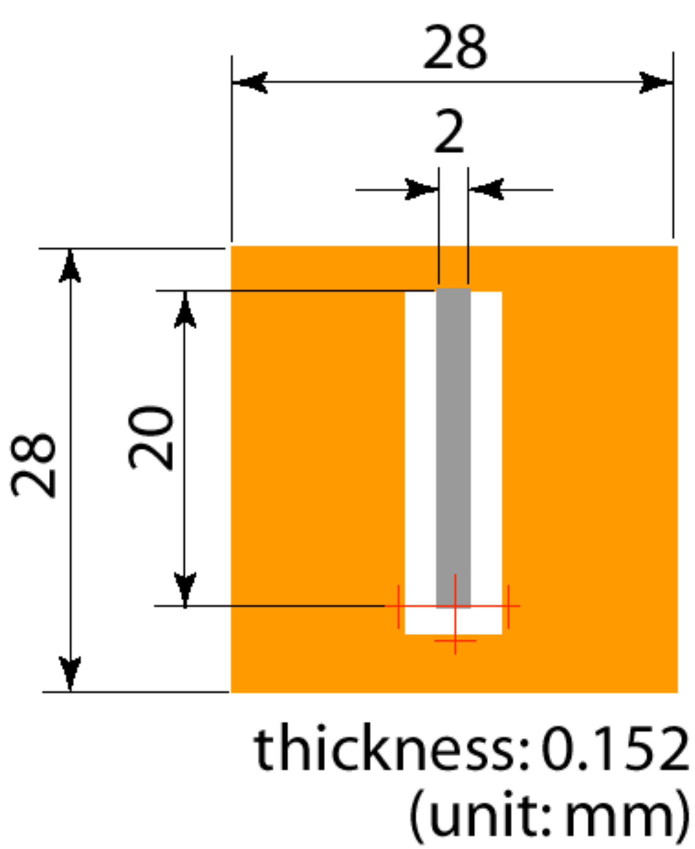
- As a higher current density:
  - observed gradually reduced and then no hillocks
  - observed hydrogen evolution (plating efficiency dropped)
  - showed a higher compressive stress
  - changed from wavy to facet grain shape
  - changed from Sn(211) to Sn(103) of the growth preferred orientation

# Sn Electrodeposit on Cu (Plate) and Phosphor Bronze (Cantilever Beam)



## Plating Conditions

- Commercial bright Sn methanesulfonate (MSA) prepared with 18.3 MΩ-cm high purity water
- Various current density: 30 - 200 mA/cm$^2$
- Anode 99.999% Sn sheet
- 200 rpm rotating cathode to reduce $H_2$ evolution effect
- Plating at 25 °C! No thermal expansion stresses!

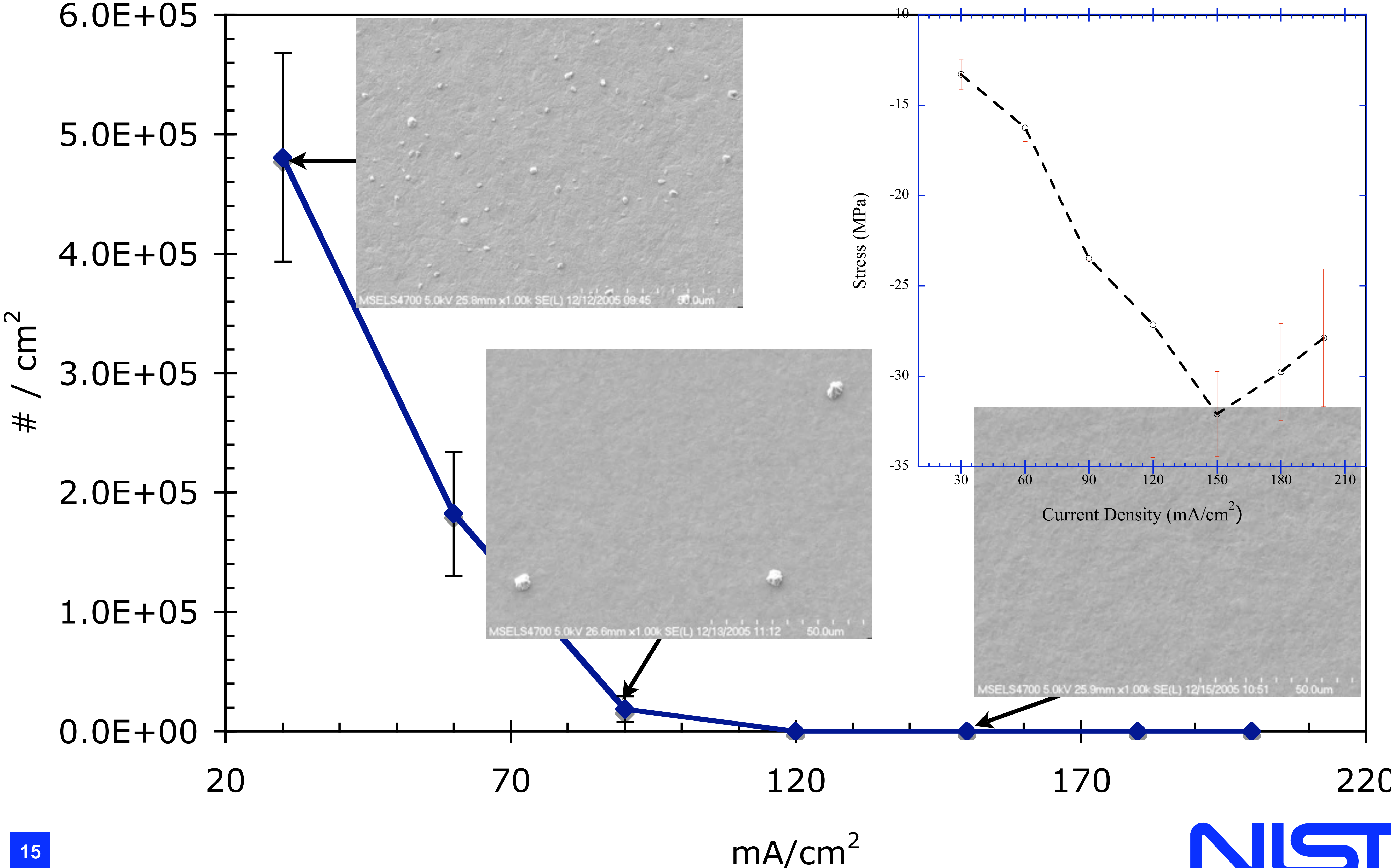



- Phosphor bronze substrate

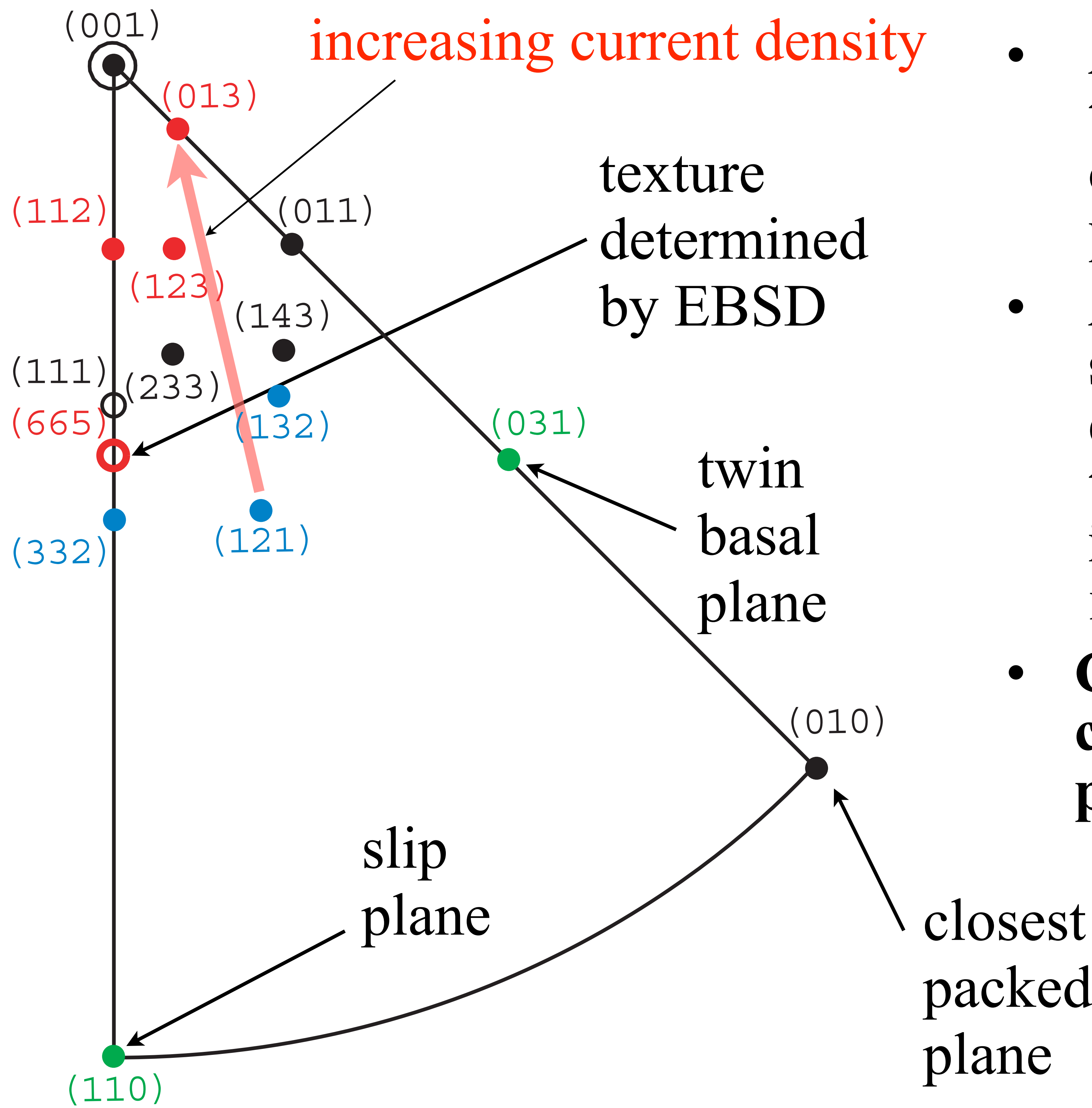
## Analysis

- SEM: surface morphology
- FEM: cross-sectional microstructure
- XRD: Preference of grain orientations
- Optical microscopy: deflection of the cantilever beam

# Hillock Density Depending on Deposit Current Densities



# Stereograph with Preference Factors of Sn Deposits and Sn Whisker/Hillock Formation




- At low stress and long time, stress relief occurs by creep processes
- At a high stress and short times, plastic deformation (slip / twinning) might be important for stress relief mechanisms
- Changes of PF might correspond to the plastic deformation



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# Indentation Stressed Sn Electrodeposit

- Evaluating whether a critical stress condition exists to grow whiskers
- Investigating whisker nucleation and growth mechanism
- Determining mechanical properties of Sn deposit
- Preparing a test method to stimulate whisker formation on Sn or Sn alloy electrodeposits



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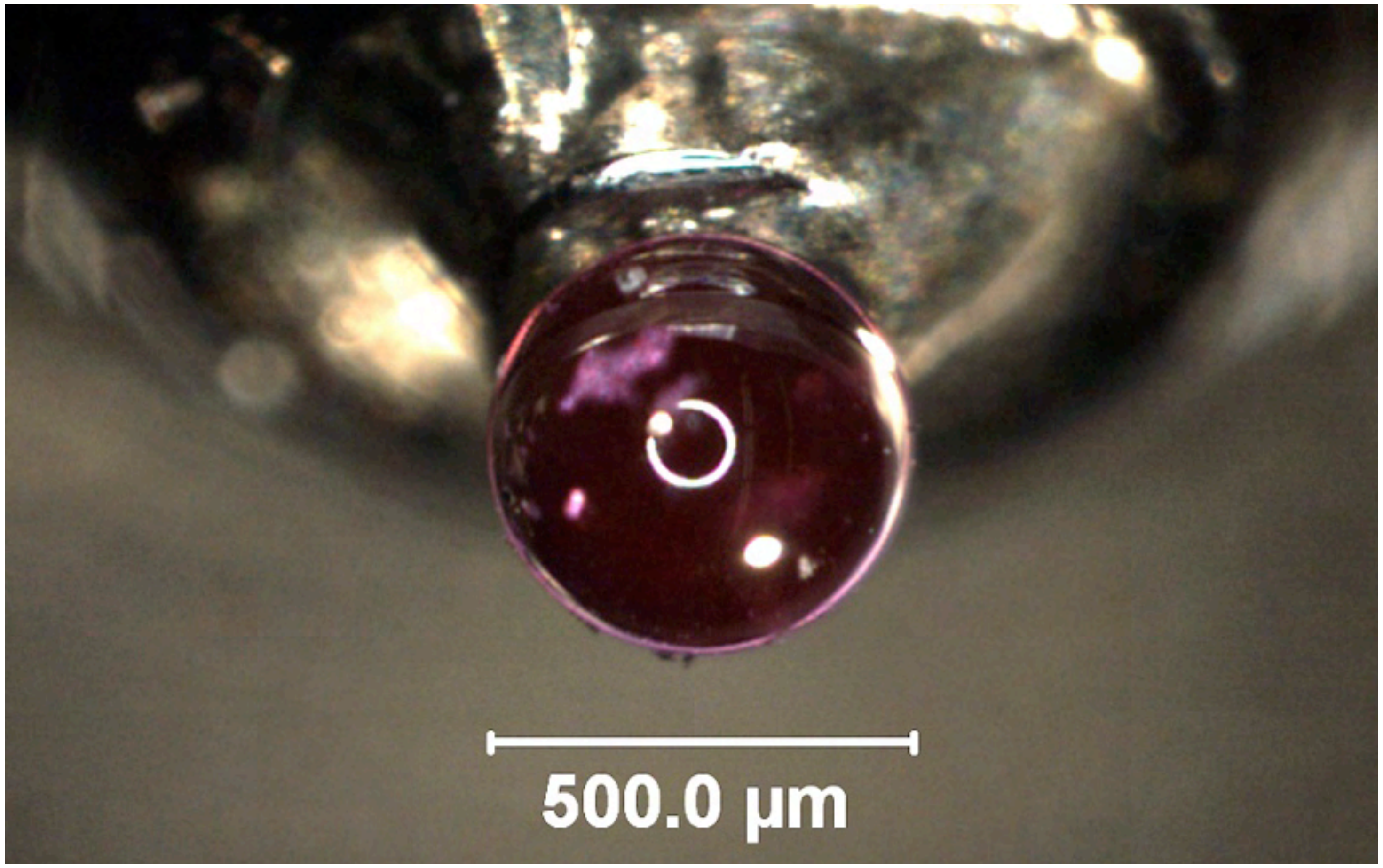
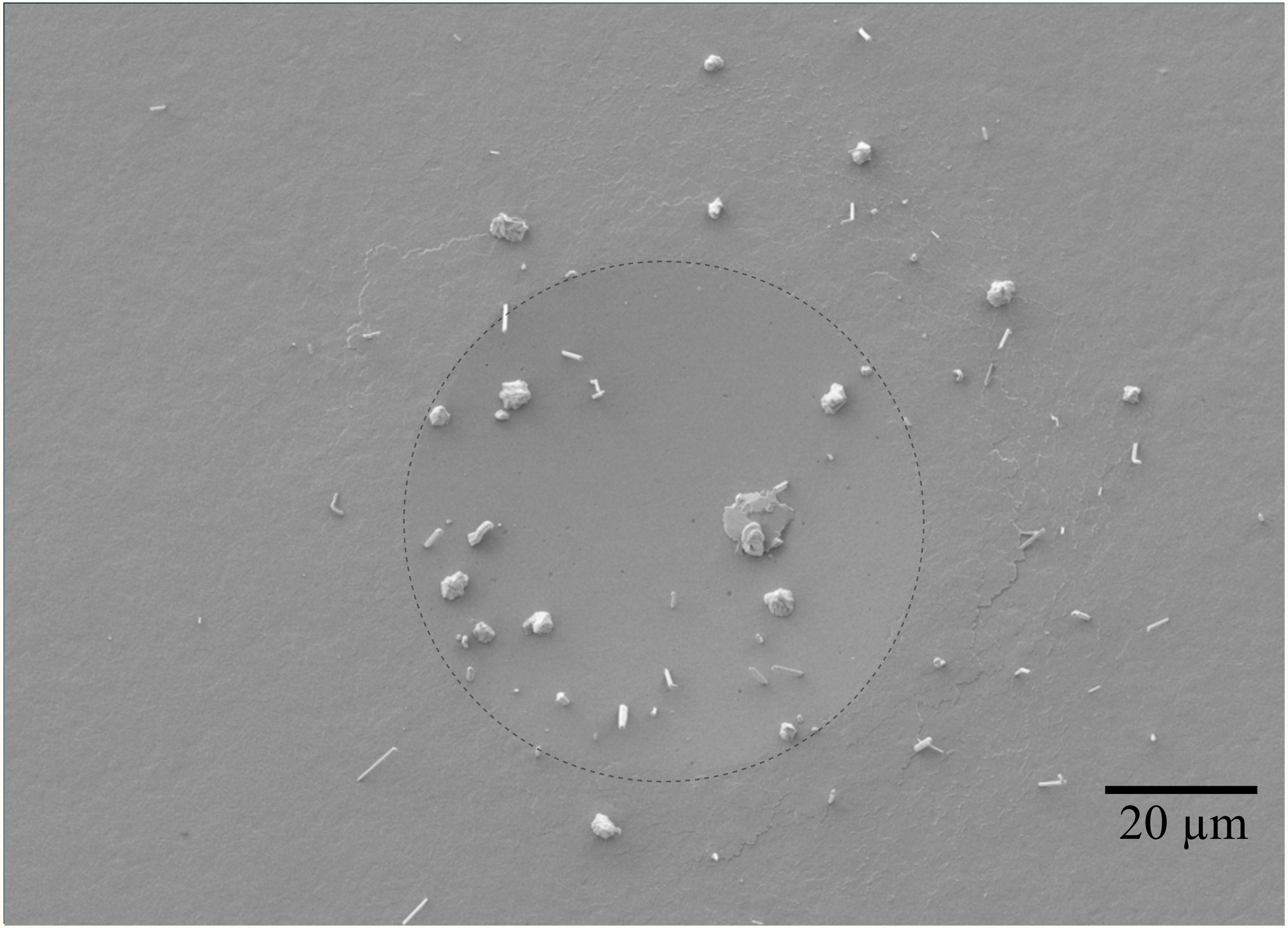
# Indentation Tests

- 15 μm thick Sn electrodeposit on 500 μm thick Cu plate
- Nano-Indenter
  - diameter: 500 μm sapphire ball
  - load: 0.2 N to 10 N

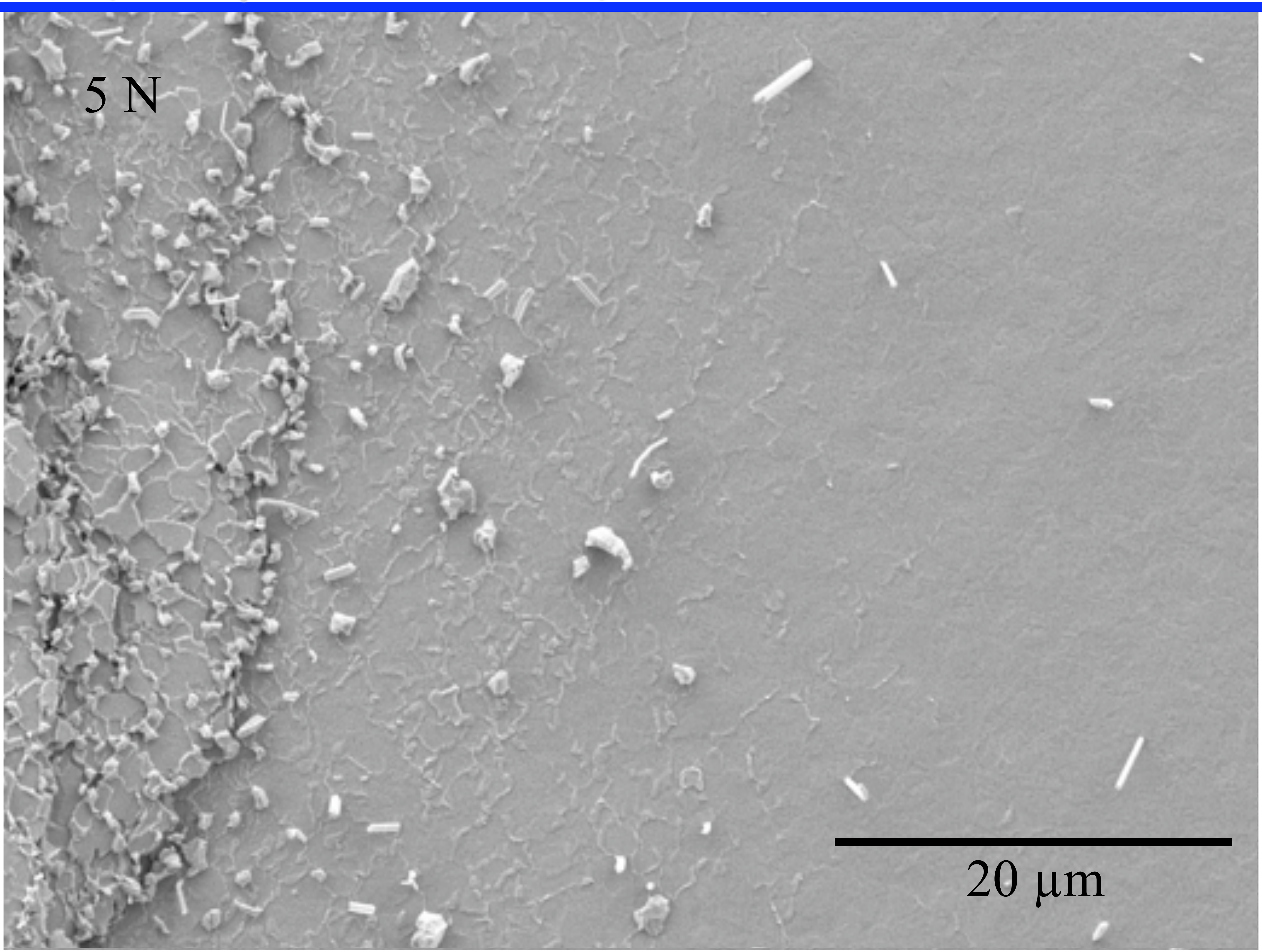


# Direct Observation of Sn Whisker Growth




- Pure Sn
- 500 µm Ball Nano-indenter
- 1 N load
- Indent depth: 1.8 µm

# Trend of Whisker Formation by Indentation Tests on Sn (500 µm Dia Ball): Load from 0.2 N to 5 N



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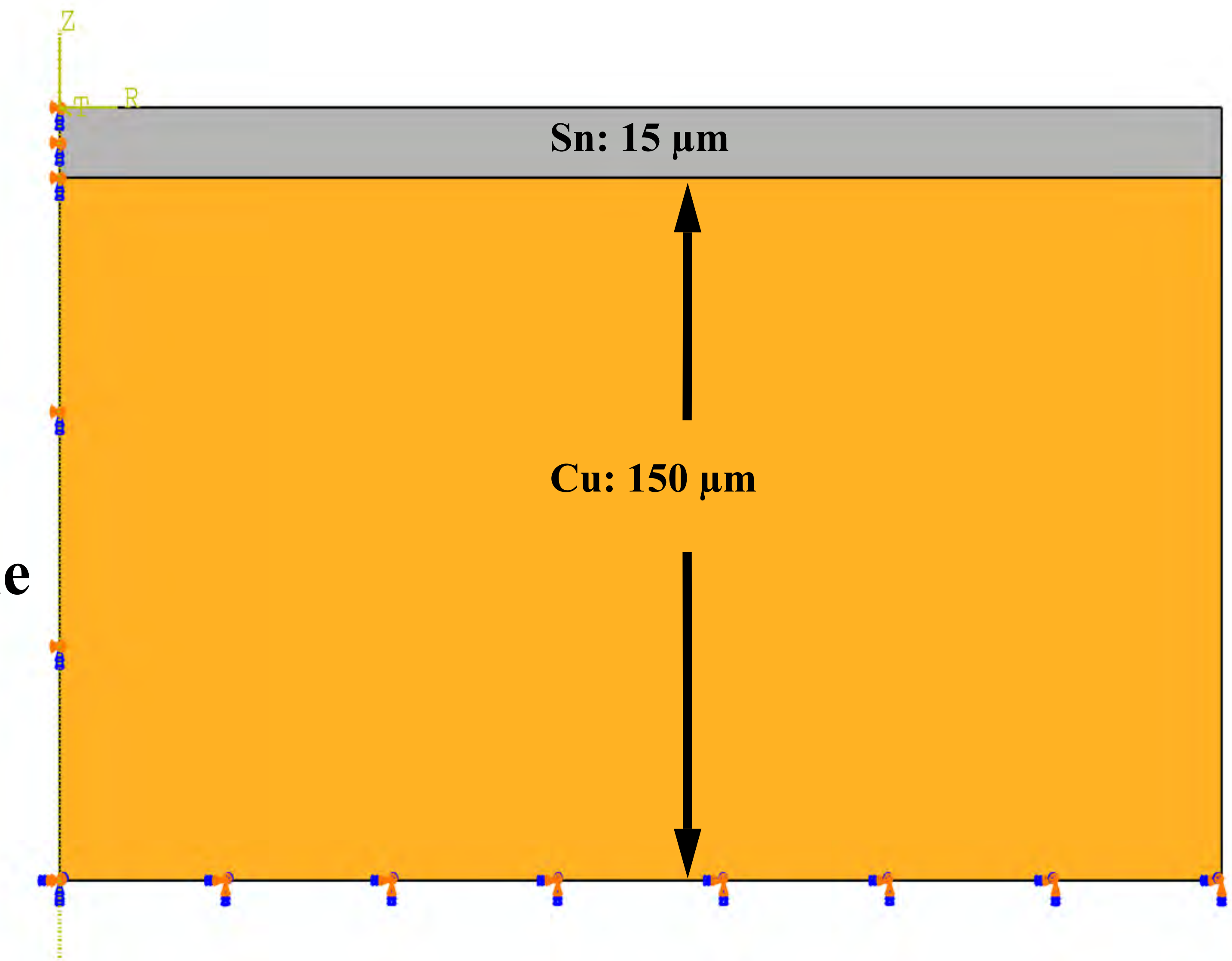
# Finite Element Modeling (Preliminary)

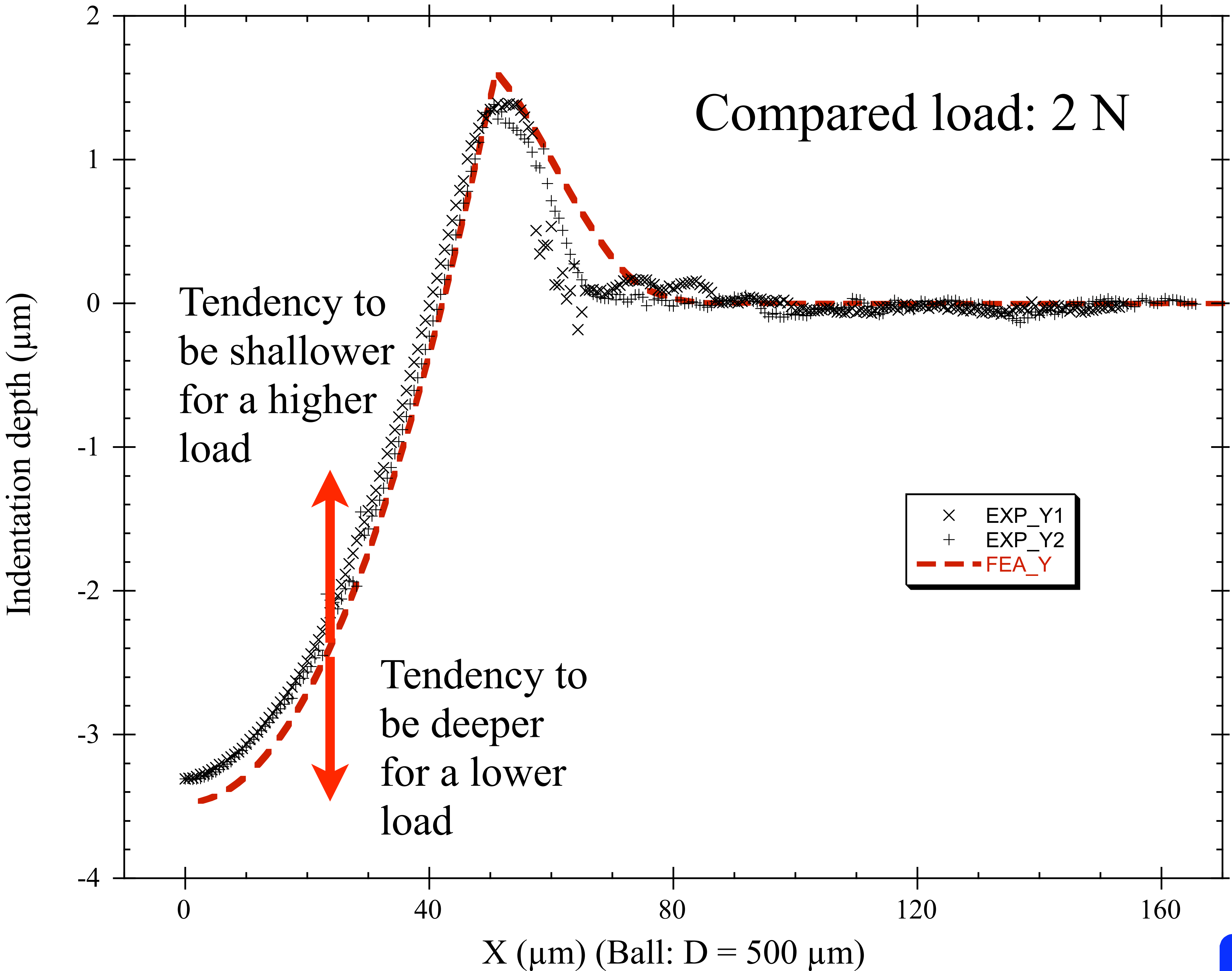
Commercial FEA software:ABAQUS

- Indenter: Rigid
  - Ball: dia 500 µm
- Sample Geometry
  - Axial symmetric: radial-axial plane
  - Tin (15 µm) & Copper (150µm): continuous displacement cross boundary




- Materials properties
  - Isotropic elastic & plastic properties
  - Copper: E =110 GPa, $\nu$ = 0.34, $\sigma_y$ = 324 MPa, $\sigma_u$ = 400 MPa
  - Tin: E = 41.4 GPa, $\nu$ = 0.33, $\sigma_y$ = 44 MPa, $\sigma_u$ = 81 MPa
- Coefficient of friction: 0.1

# Validation of Sn Properties (Preliminary) by Comparing Indentation Shape and FEA Model



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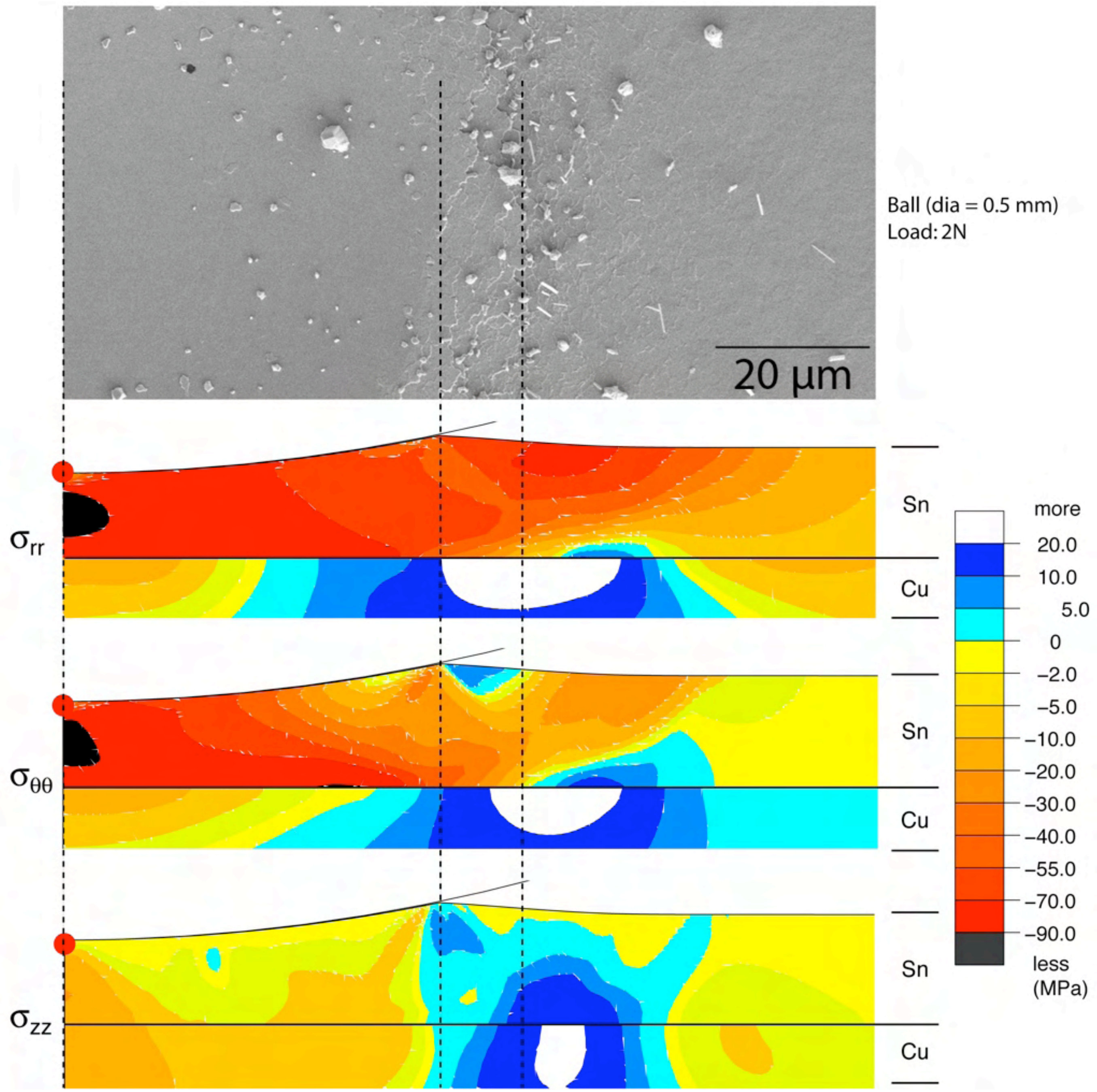
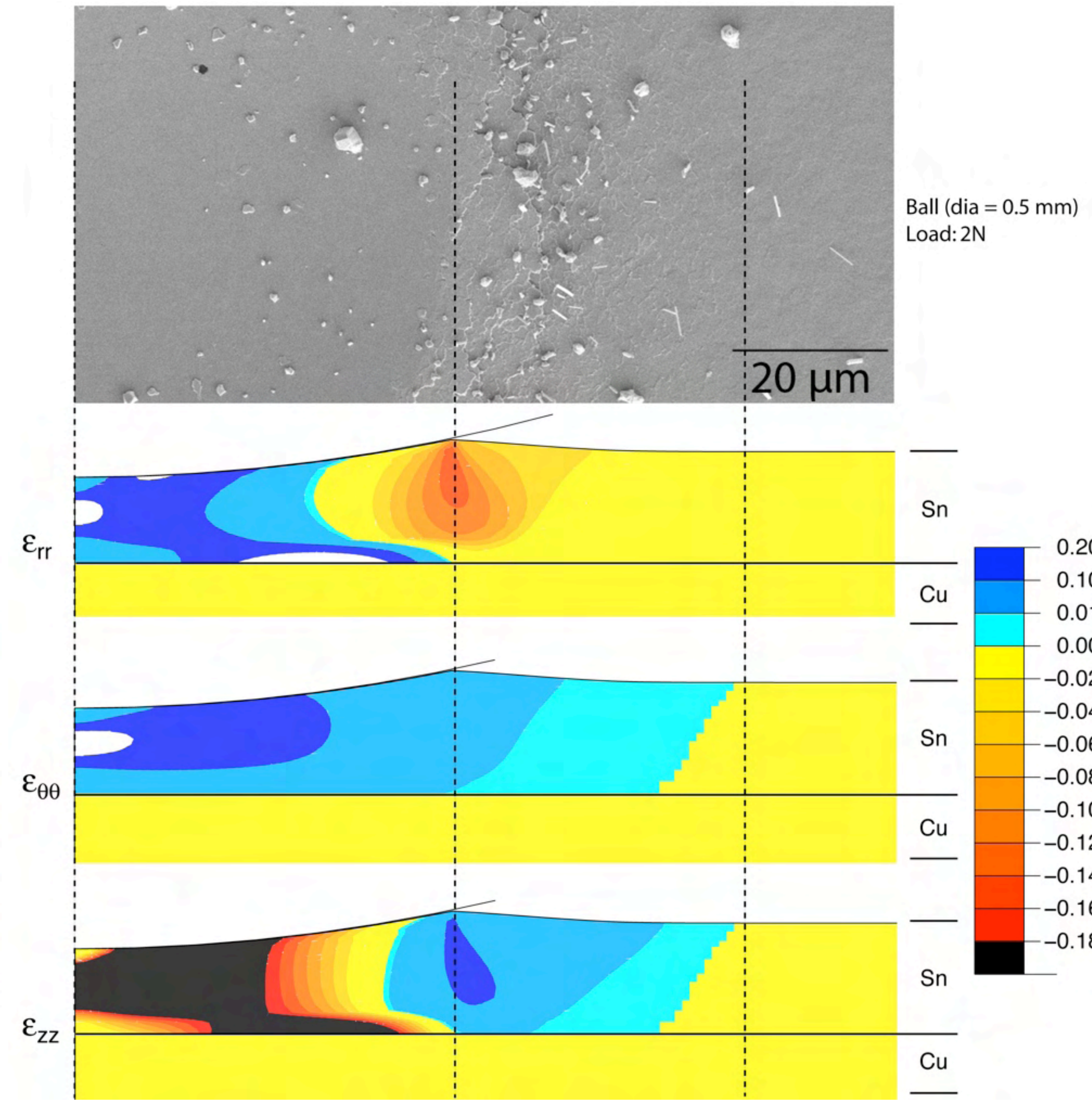
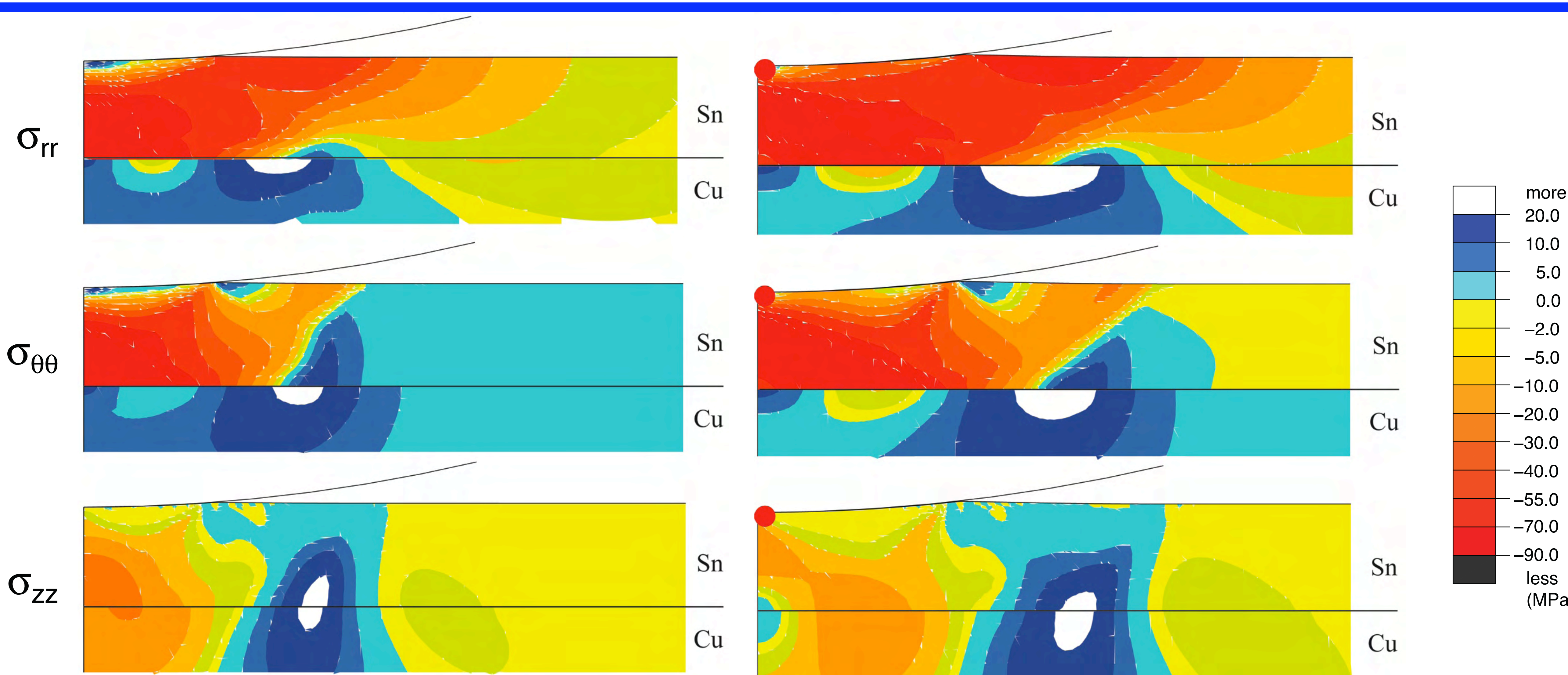
# Stimulation of Sn Whisker Formation: FEA for the 500 μm Dia Ball Indenter (unloading)

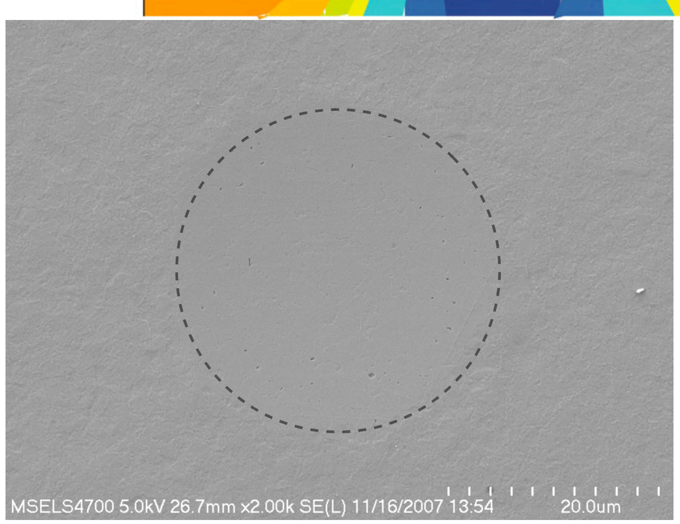


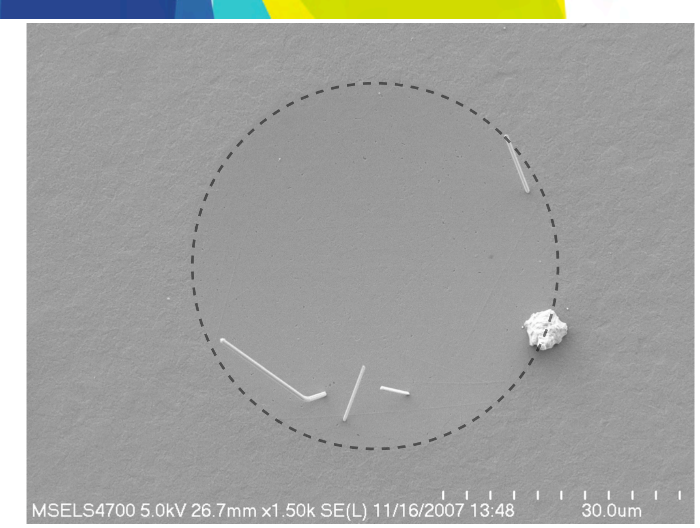

$\sigma_{rr}$ & $\sigma_{\theta\theta}$ should be compressive

# Minimal Conditions of Stress Components to Form Whiskers

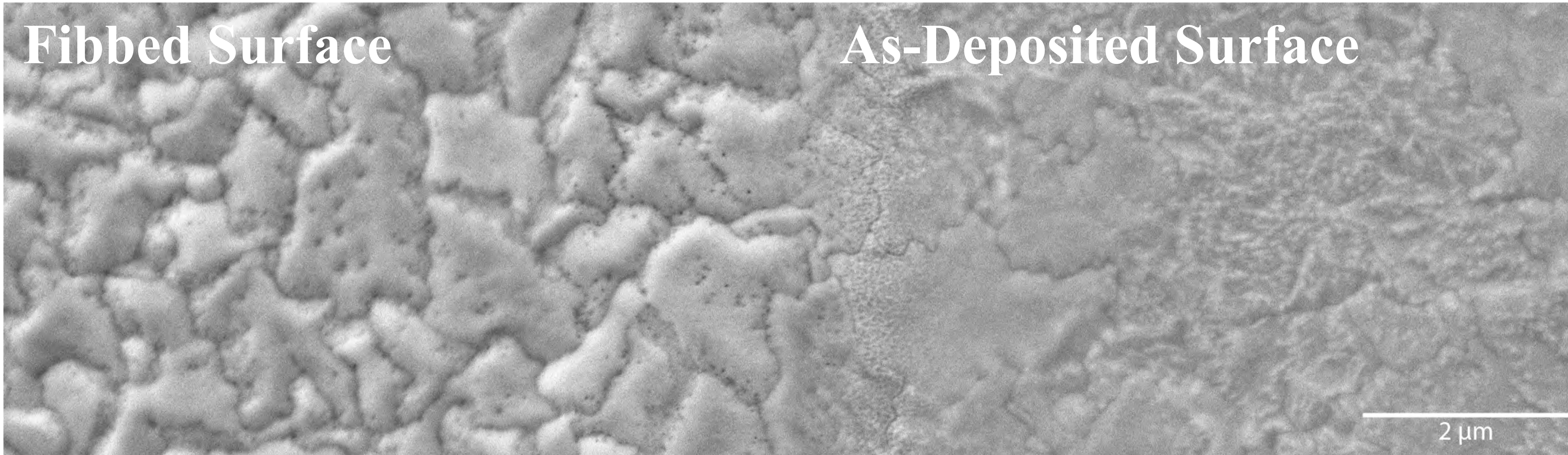



- $\sigma_{rr} < -10$ MPa
- $\sigma_{\theta\theta} < -2$ MPa
- $\sigma_{zz} < 0$ MPa



# Surface Layer and Sn Whisker Formation






**Nano-indentation tested with 500µm dia and 1N load**

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# Summary of Indentation Stressed Sn Deposits

- Successfully grown whiskers by the 500 µm ball indenter
- The minimal stress conditions to grow whiskers were
  - $\sigma_{rr} < -10$ MPa
  - $\sigma_{\theta\theta} < -2$ MPa
  - $\sigma_{zz} < 0$ MPa
- A further precise FEA was demanded
  - Determine Sn electrodeposit mechanical properties: E, σ, and $\sigma_u$
  - Determine the coefficient of friction
  - Consider:
    - dynamic creep phenomena
    - stress gradient in the film
    - mechanical strength of the surface layer



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# Future Work for Sn Whiskers @ NIST

- Mitigation strategies - modify grain structure or other….
- Test method for whisker likelihood
- Do direct measurements of stress in Sn (lattice parameter) agree with deflection measurements/ model
- What causes nucleation/localization of flow
- Mechanism of whisker curve/kink
- Artificial stimulation of whiskers
- Coupling of hillock formation and grain boundary motion
- Cause of intrinsic plating stress
- Role of grain boundary sliding
- Surface grain structure and anisotropy of Sn