How do whiskers and hillocks grow in Pb-free Sn coatings?

Fundamental mechanisms controlling stress evolution and whisker growth

Eric Chason, Nitin Jadhav, Eric Buchvecky, Allan Bower, Sharvan Kumar

Brown University, Div. of Engineering

SMTA 2010 Orlando, Fl

- Sn (Pb-Sn alloys) coatings on Cu used commonly by electronics industry
    - Solderability/oxidation resistance

- Push towards Pb-free manufacturing
    - RoHS

- Problem: Pure Sn forms whiskers on Cu
    - Failures in satellites, pacemakers, missiles
    - http://nepp.nasa.gov/whisker

- Driving force believed to be stress from IMC
    - But details not understood

Sn or Pb-Sn
Cu

2 μm
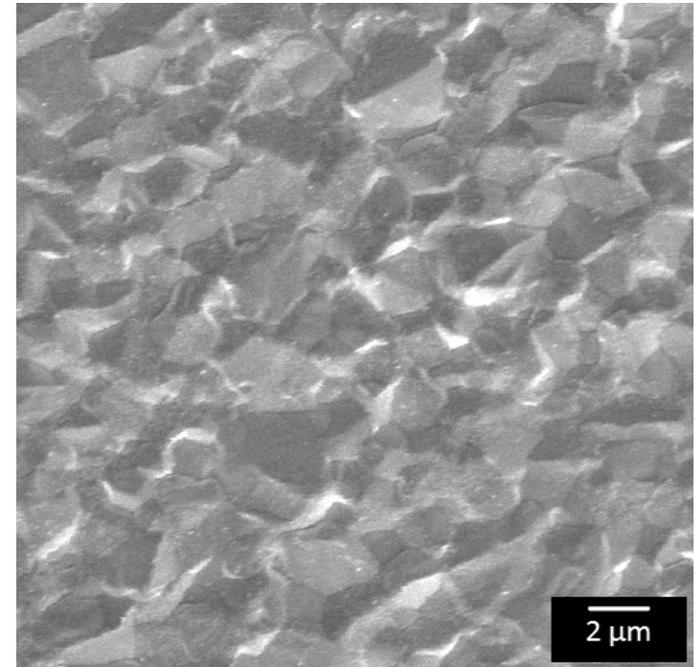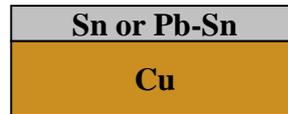
Real-time SEM measurements (4 days)
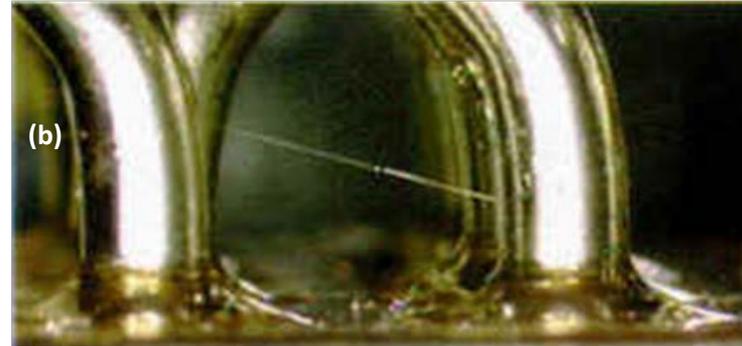
Examples of whisker failures

NASA website: http://nepp.nasa.gov/whisker
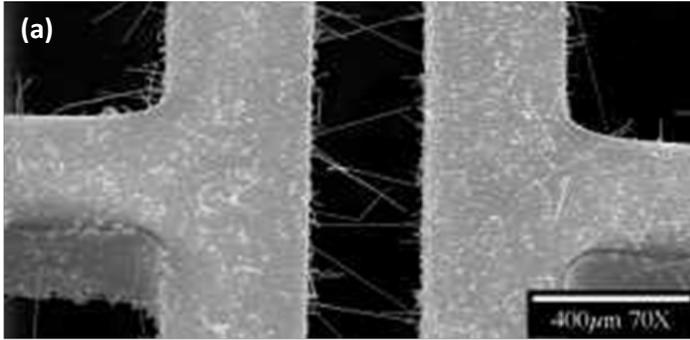
MATTE tin-plated copper lead frame after 3 years of ambient storage
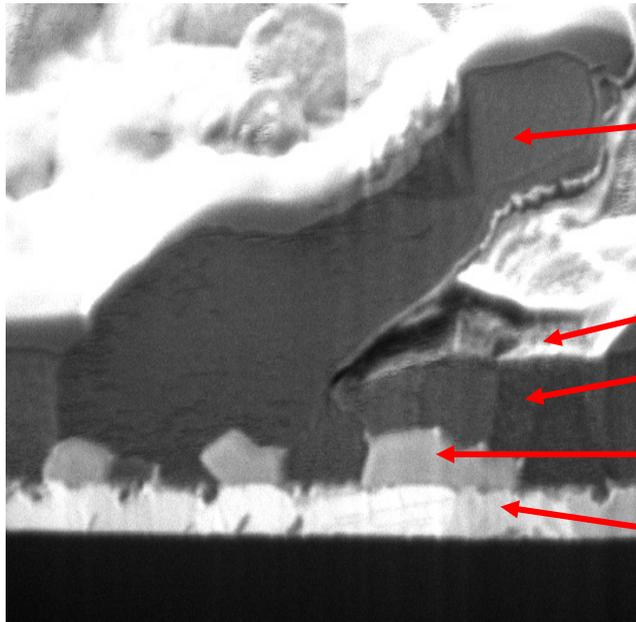

Terminal of a Sn plated relay

Card guide in space shuttle flight box

Relay destroyed by suspected tin whisker-induced metal vapor arc

Difficulty: Multiple materials processes control whisker formation

whisker

oxide

Sn

IMC

Cu

- Complex multilayer structure with multiple phases
- Sn, Cu, IMC, oxide

- Many kinetic processes to consider:
- microstructural evolution
- (inter)diffusion of Sn, Cu
- intermetallic growth
- stress generation in Sn
- whisker nucleation and growth

- Lots of prior and ongoing work
- many systems/processing methods

Approach: Use systematic measurements to identify mechanisms/develop models

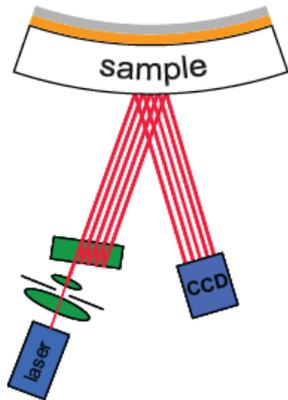**Understand**: How does stress relate to IMC growth?

How does stress lead to whisker formation?
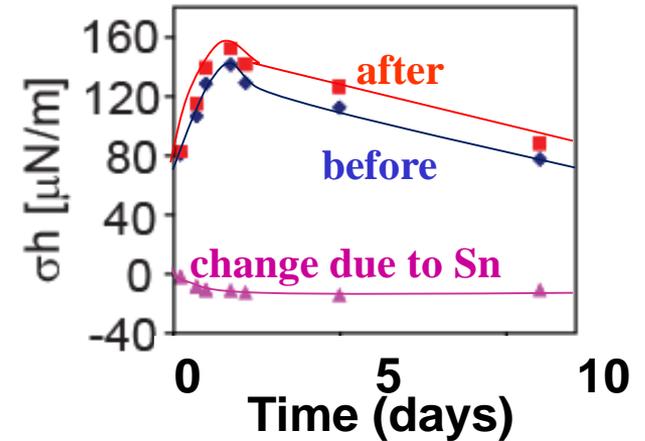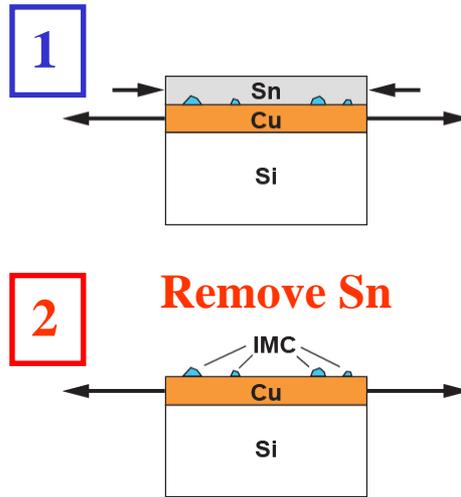
How do whiskers grow?

# Quantify kinetics of stress/IMC/whiskers in real-time
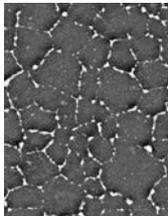
1) *Stress evolution*

Wafer curvature measures *total* force exerted by film.

1

2 **Remove Sn**

σh [$\mu N/m$] vs Time (days)

after
before
change due to Sn

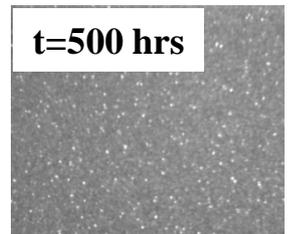Remove Sn layer – change in curvature gives stress in Sn

2) *IMC volume*

Selectively etch Sn

Find IMC volume from mass change

Also IMC morphology

IMC Vol./Area (nm)

3) *Whisker density*

t=0 hrs

t=500 hrs
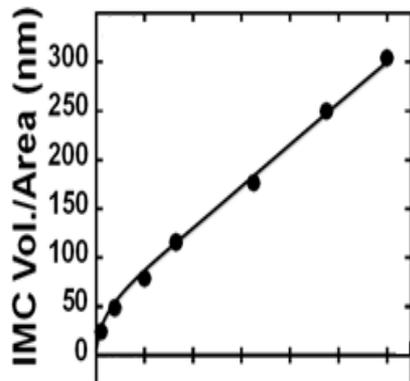
Oblique illumination highlights whiskers

optical micro-scope

light
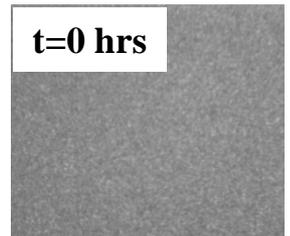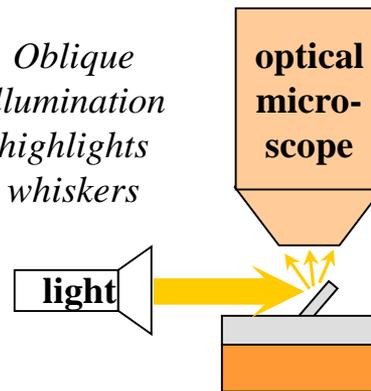
Correlate stress/whiskering with IMC growth

Pure Sn on Cu

Sn
Cu
Si
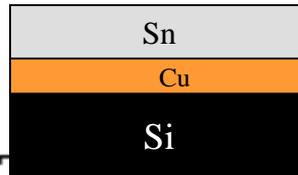
Samples: Electrodeposited
1.2 micron Sn/0.6 micron Cu
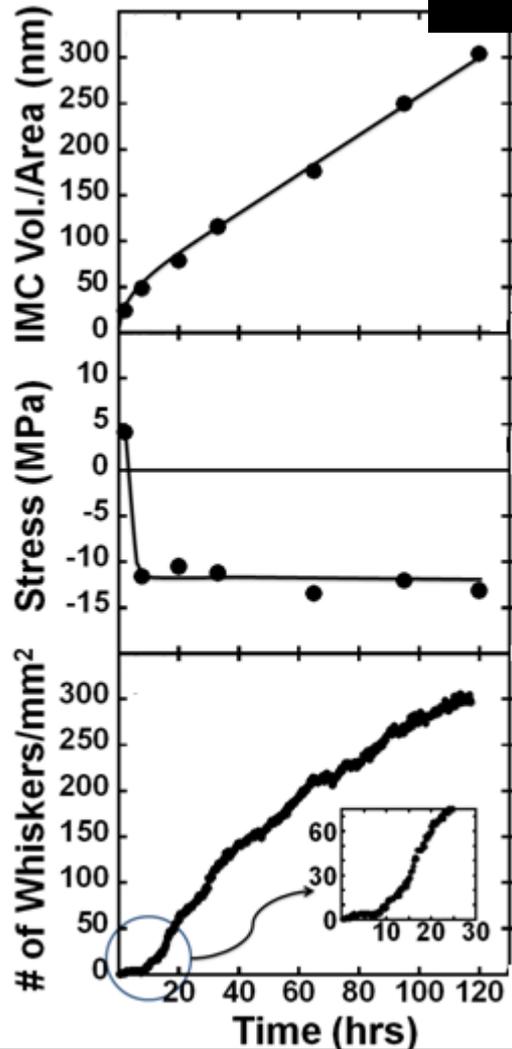
Pure Sn overlayers

- IMC grows continuously (rate slows with time)

- Stress saturates soon after formation of IMC (~12 MPa)

→ Onset of plastic deformation

- Whiskers start to grow after stress saturates (seen in SEM too)

- Have also studied effects of grain size, layer thickness, Pb alloying, annealing (next talk)
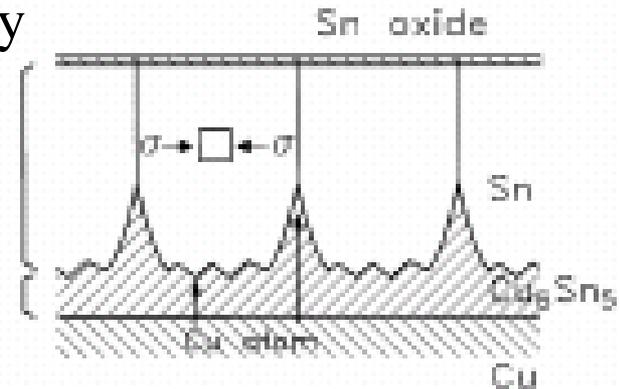
What are the mechanisms controlling stress?

"Standard picture": IMC grows into grain boundary
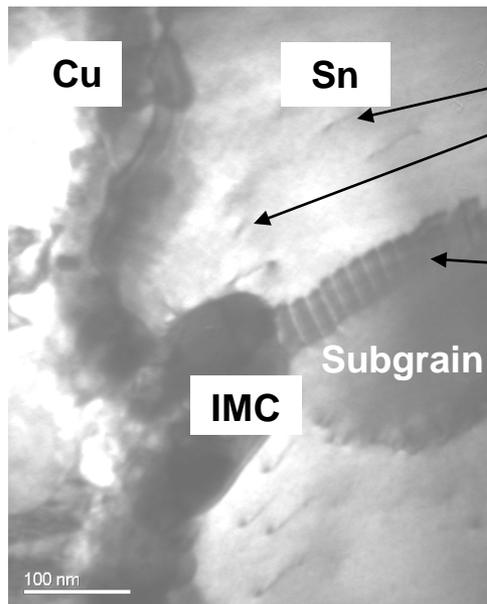 Creates stress in Sn layer (Lee and Lee,1998)

→ *Must be more than elastic effects*

- *Stress exceeds yield stress*
- ***Need to consider plastic deformation***

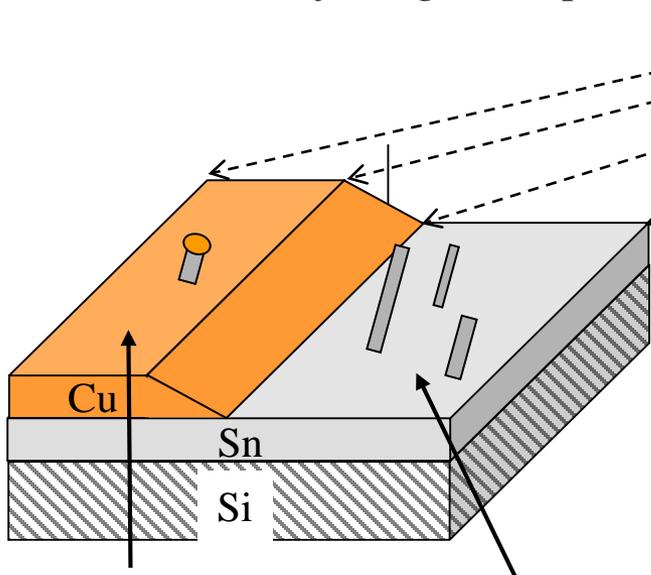## Stress relaxation by dislocation formation (X-TEM)

(Kumar, JMR 2008)

Extensive dislocation
emission around IMC particles
  - *transmits strain into*
    Sn layer

Dislocations form into
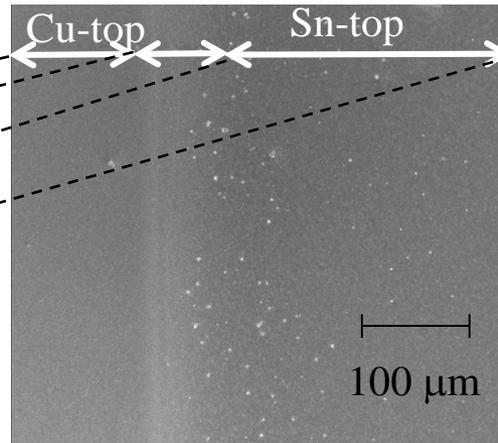subgrain boundaries (highly
mobile)

Stress relaxation by grain boundary diffusion: "ledge sample"

Schematic of ledge sample
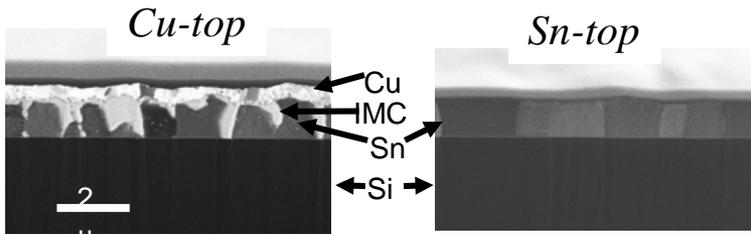
SEM around ledge

(Reinbold, JMR 2009)

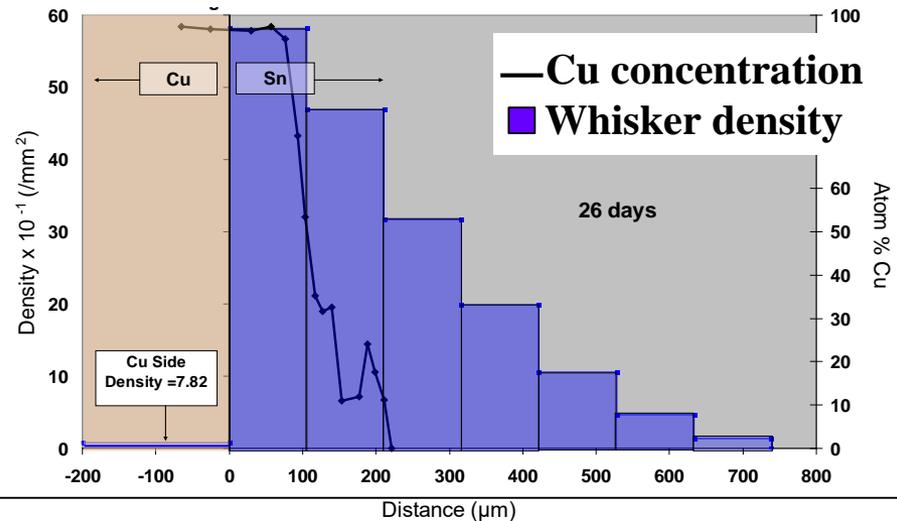Cu-top | Sn-top

100 µm

Cu

Sn

Si

- "Ledge": Deposit Cu over **half** of Sn layer

- Monitor whisker density with SEM

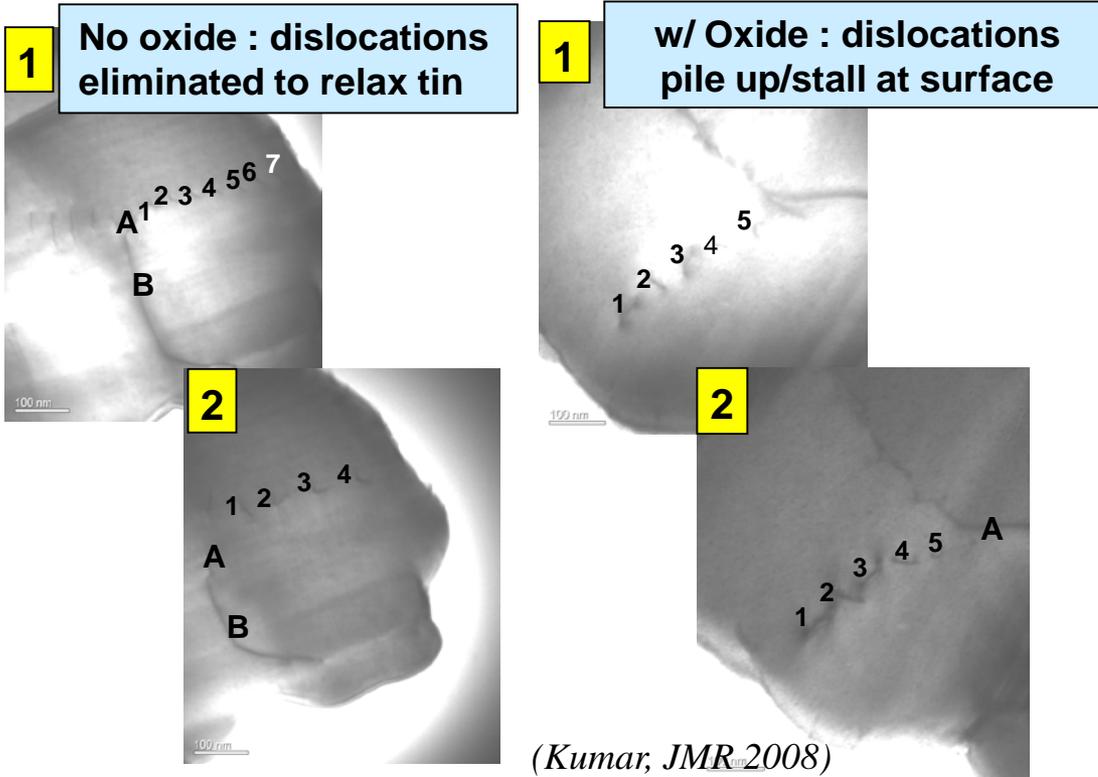- Measure Cu evolution with EDS

- Whiskers form farther out than IMC

Cu-top

Sn-top

Cu
IMC
Sn
Si

2

FIB images of ledge sample
- *No IMC 700 microns from ledge*
- *But whiskers are seen*

Cu

Sn

26 days

Cu Side
Density =7.82

—Cu concentration
■ Whisker density

Density x 10^{-1} /(mm^2)

Atom % Cu

Distance (µm)

Surface oxide prevents stress relaxation at surface

TEM shows dislocation pile-up at oxide

1 No oxide : dislocations eliminated to relax tin

1 w/ Oxide : dislocations pile up/stall at surface

2

2

(Kumar, JMR 2008)

Stress relaxes when oxide removed *(Chason, APL 2008)*

oxide

Sn

Cu

Si substrate
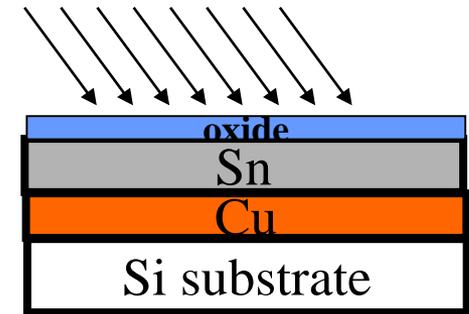
Remove oxide by:
- Sputtering surface in vacuum
- Etching surface in solution

**Curvature shows irreversible change due to stress relaxation in Sn**

Stress-thickness (MPa-m)

Sputter beam on

Time
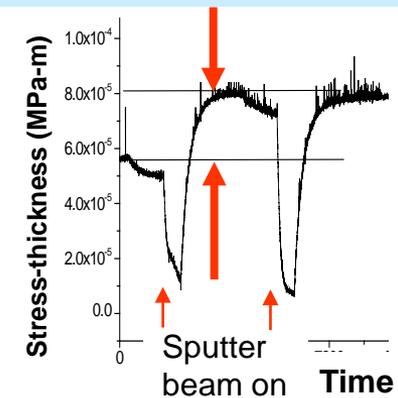
Put these mechanisms into model using finite element analysis (FEA)
## *(informed by experiments)*

Features of model:

- **Polycrystalline Sn film**
- **Columnar microstructure in Sn**
- **Cu substrate (homogeneous)**
- **IMC expansion** at Sn/Cu interface (matched to measured V_{IMC} vs. time)
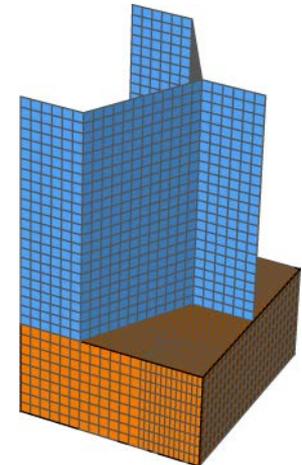
Mechanical behavior:

- **Elastic deformation (isotropic)**
- **Plastic deformation** (isotropic)
- **Stress-driven, grain-boundary diffusion**
- **No surface diffusion** (effect of **surface oxide**)

periodic model cell
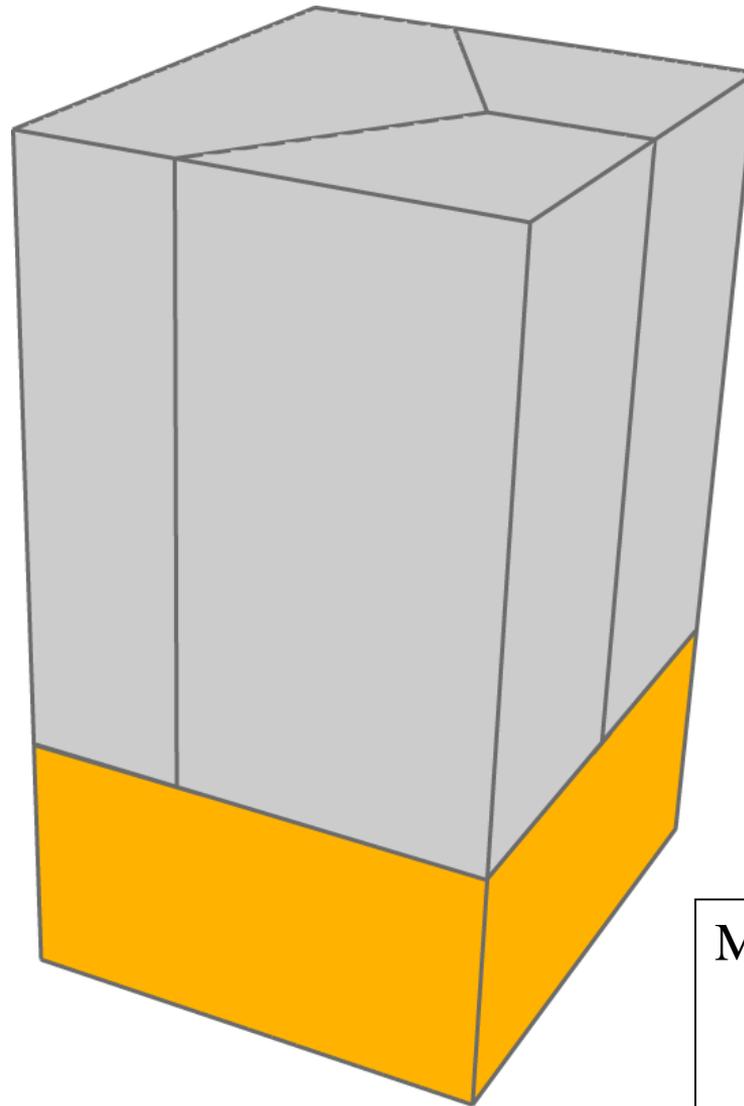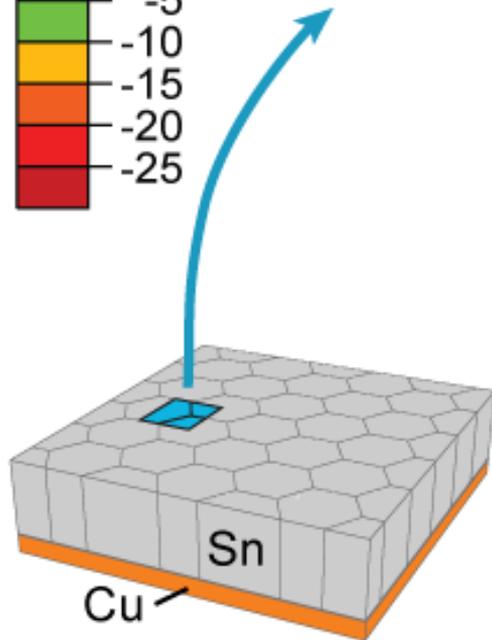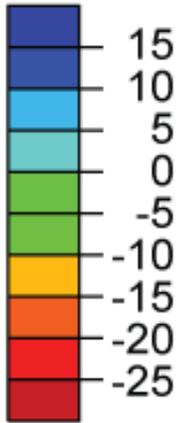
Sn

Cu
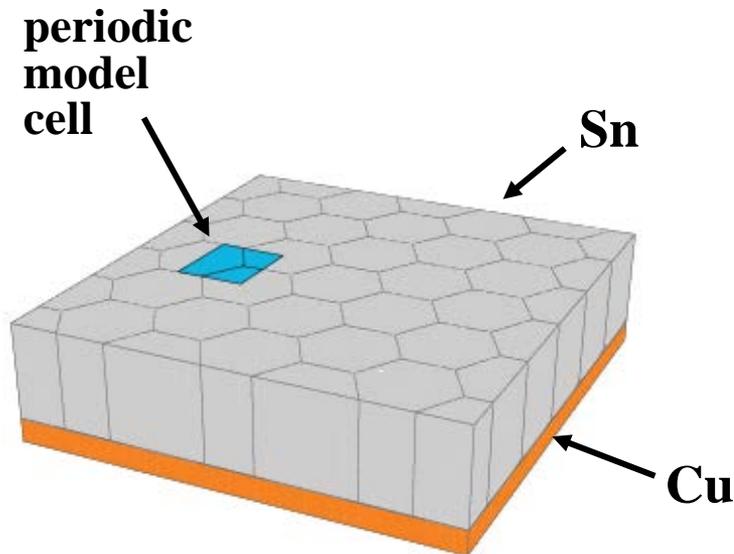
IMC expansion
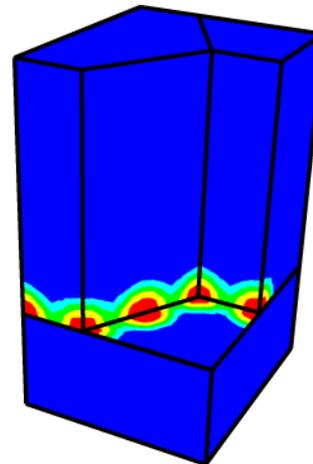
Grain-boundary diffusion elements
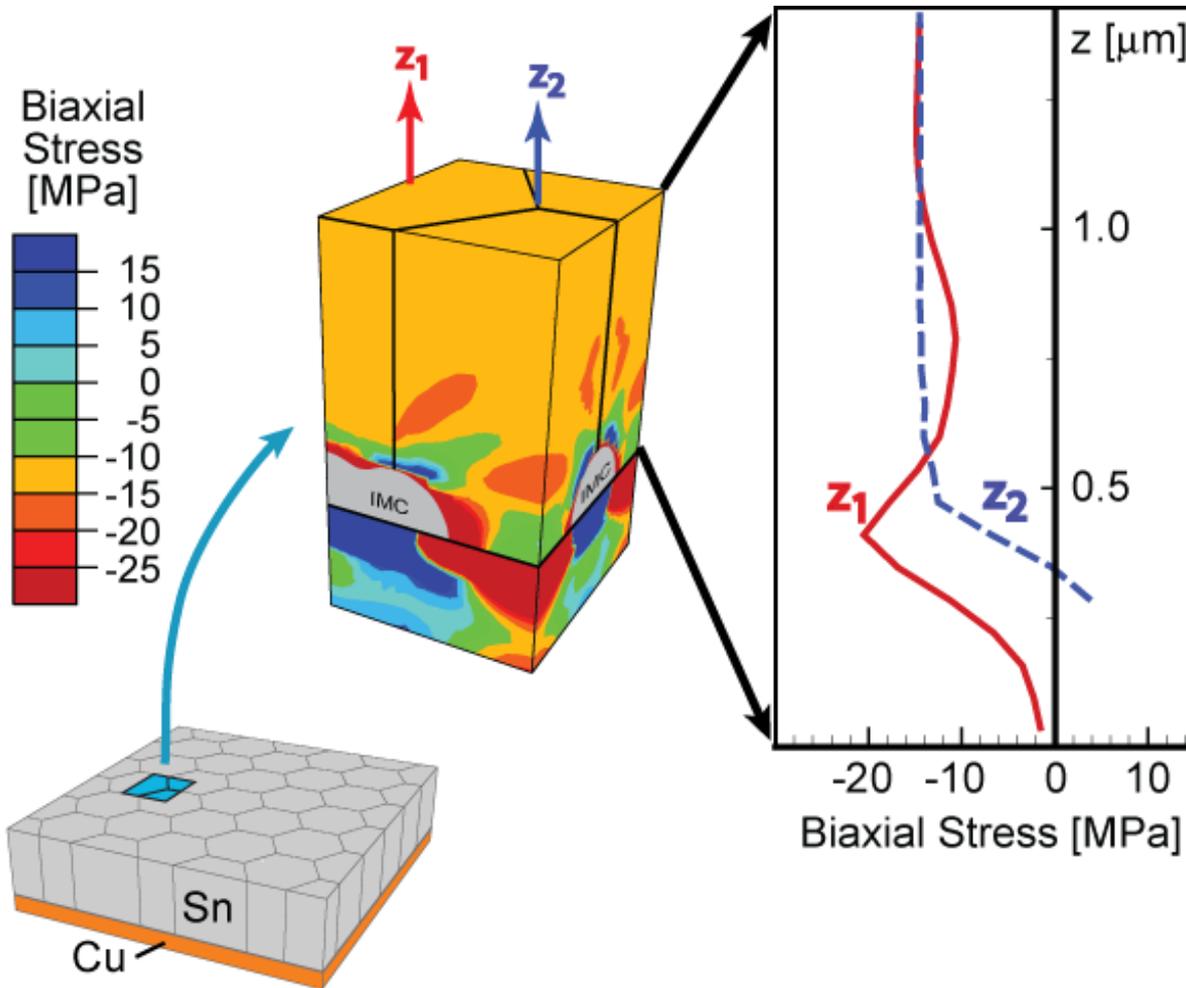
Calculate stress in Sn as IMC grows

(Buchovecky, JEM, 2009)

Mechanisms:
  -elasticity
  -plasticity
  - g.b. diffusion

# Coupled grain boundary diffusion and plastic deformation transmit stress through Sn film

With GB diffusion:

- **IMC expands at Cu/Sn interface**

- **g.b. diffusion/plasticity makes compressive stress spread upward through the film.**

- **Stress through film is relatively uniform.**

- **Full thickness of film can reach yield stress.**

(Buchovecky, JEM, 2009)

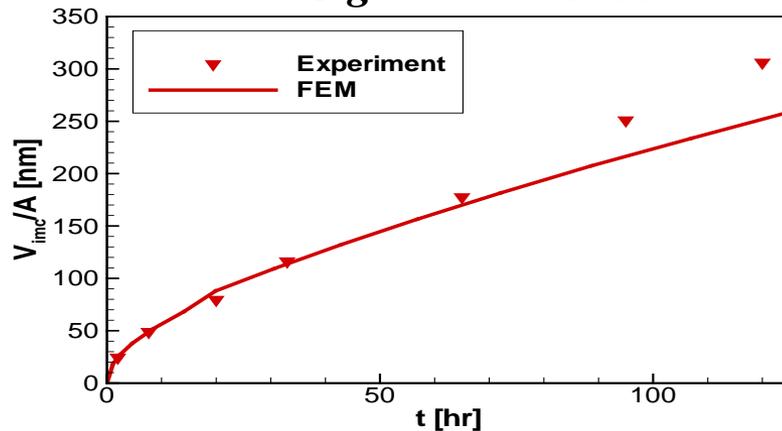# Without GB diffusion, little stress is transmitted through Sn
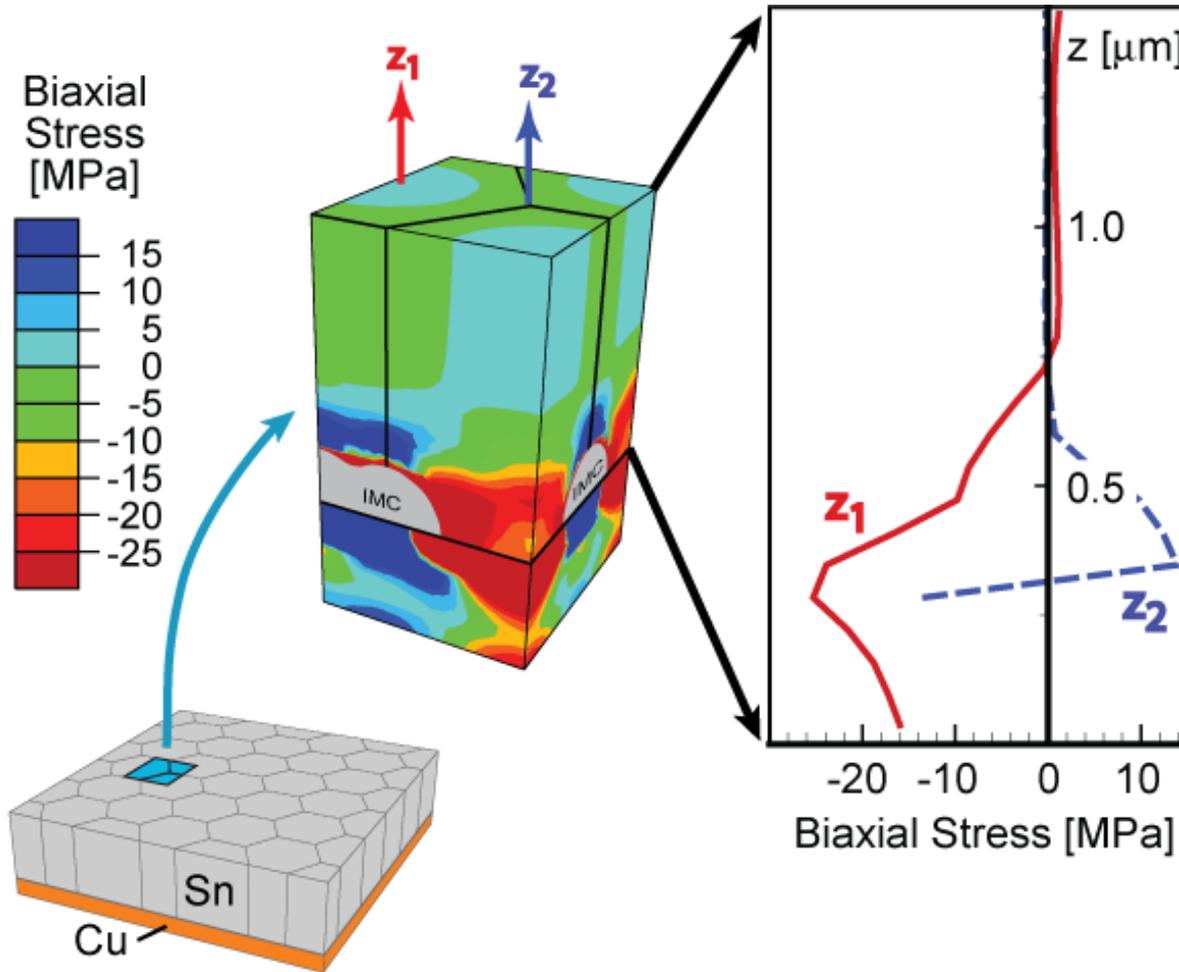
Without GB diffusion:

- **Compressive stress localized near IMC.**

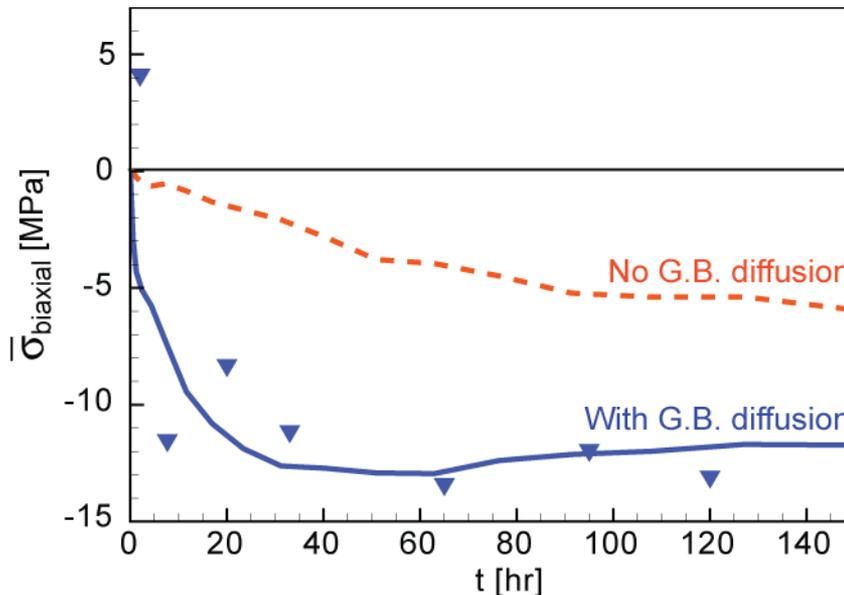- **Very low stress in much of the Sn, especially near surface.**

(Buchovecky, JEM, 2009)

Evolution of average stress with different relaxation mechanisms

IMC growth kinetics

Average stress in Sn from FEA

- Use IMC growth kinetics from experiments

- Calculate average stress over Sn thickness (as in curvature data)
  - *with g.b. diffusion*
  - *without g.b. diffusion*

- Elastic/plastic with g.b. diffusion similar to measurements
  - *Rapid rise then saturation*
  - *Stress spread across Sn layer*

FEA & measurements:
 - **Stress spreads across Sn**
      as IMC grows
 - **Due to plasticity and g.b. diffusion**
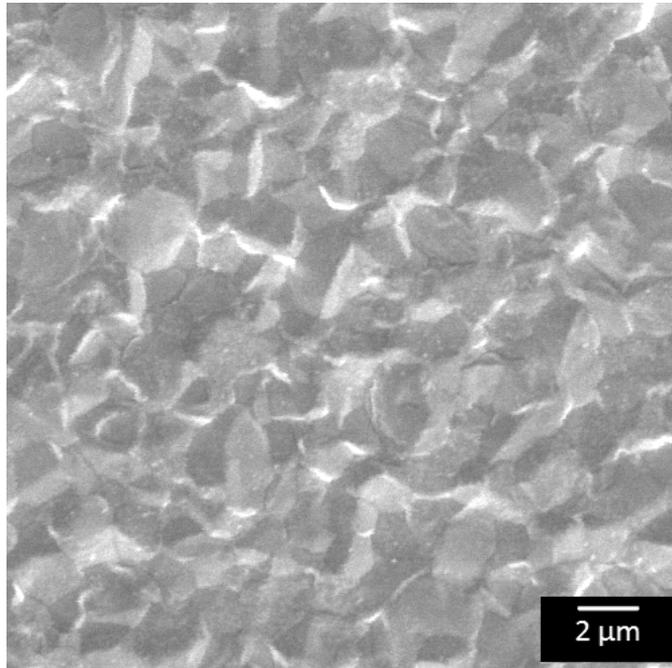 - **Saturates even w/o whiskers**

How do whiskers actually grow?

Sn (2 micron)

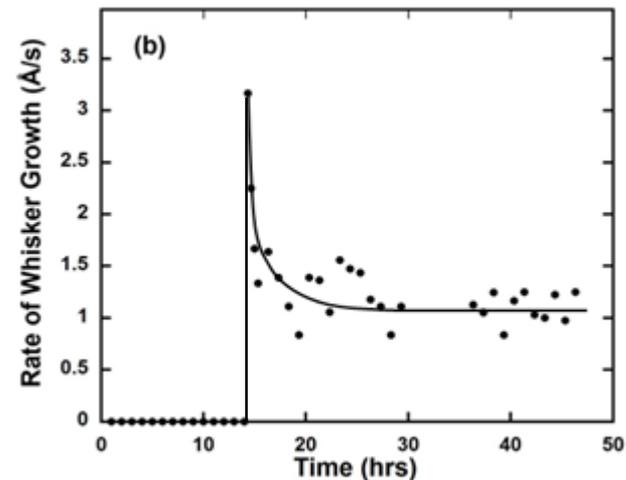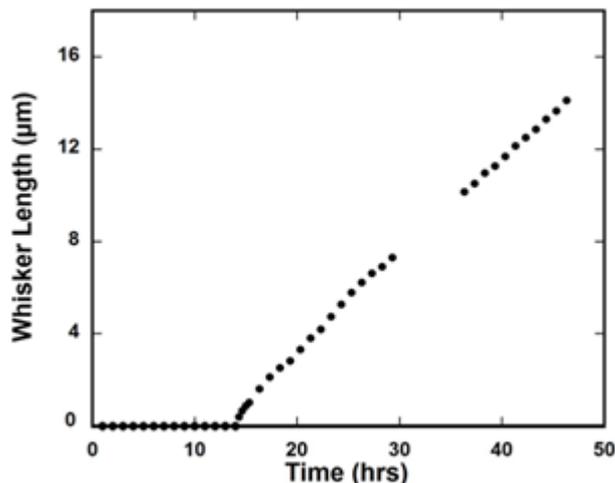Cu (1 micron)

Silicon

Movie #1


2 μm

**Real-time SEM/FIB**

(see videos at:

www.engin.brown.edu/Faculty/

Chason/research/whisker.html)

- – **Incubation period of 12-13 hrs**
- – **Whisker appears from single small grain**
- - **Uniform growth rate in vacuum**
- - **No prior surface defect before whisker nucleation**

Nucleation not due to grains with weaker oxide layer

- Sputtered off oxide using FIB
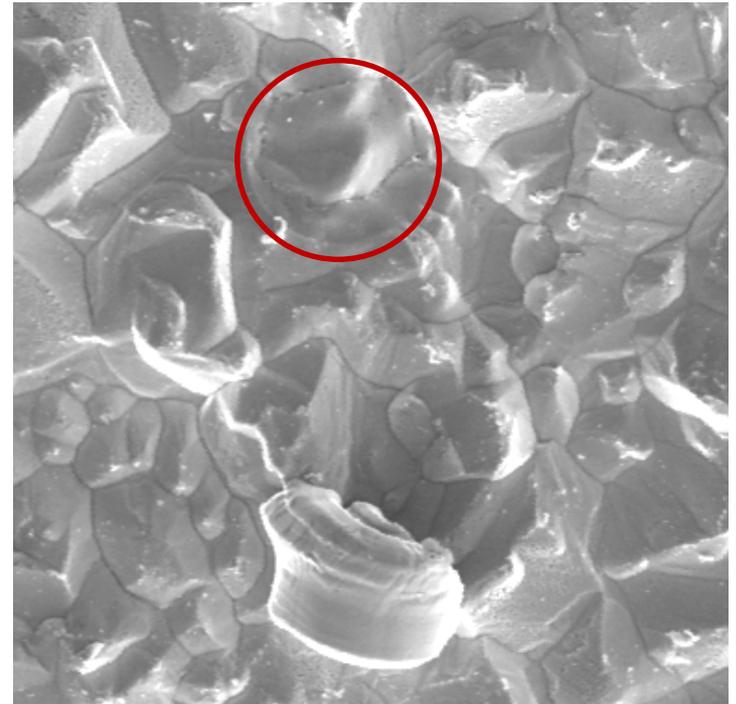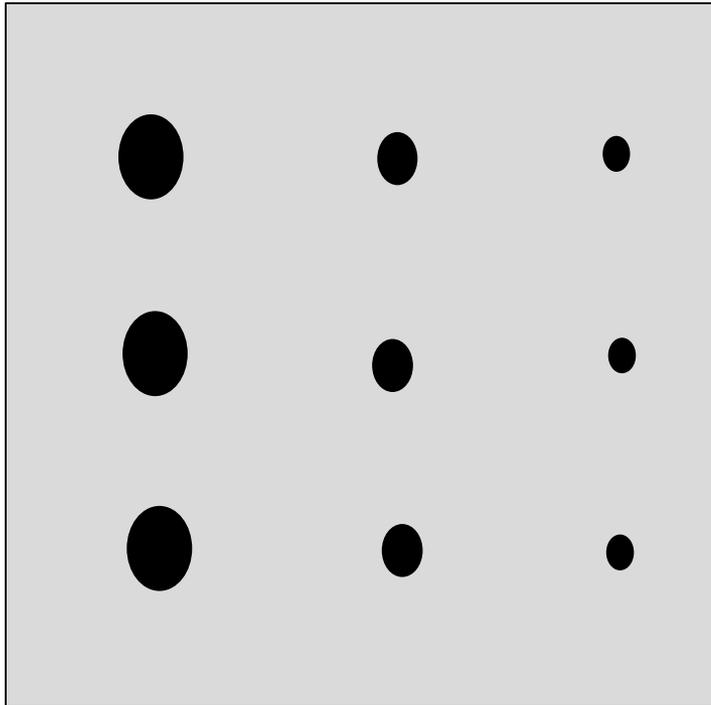   - 3 *3 array of holes of size .5,2 and 5 micron
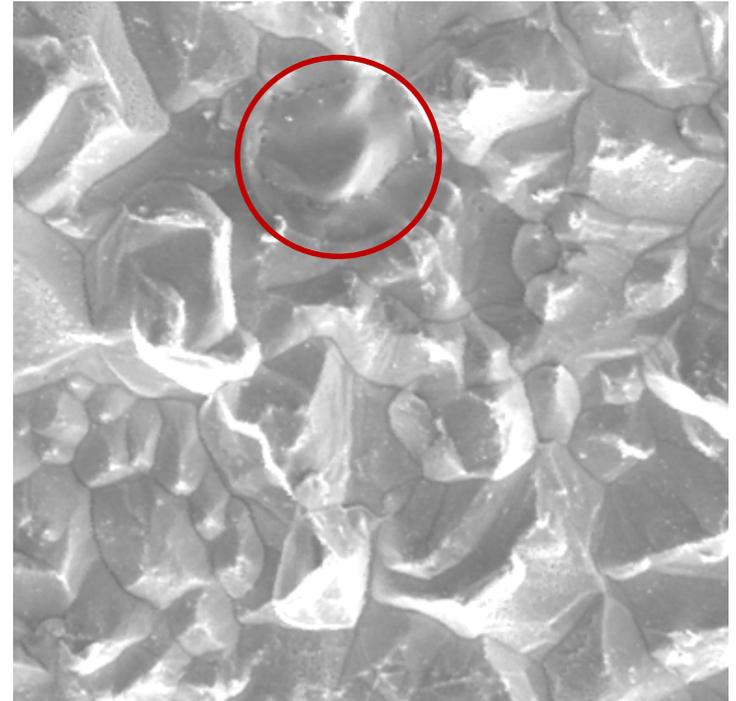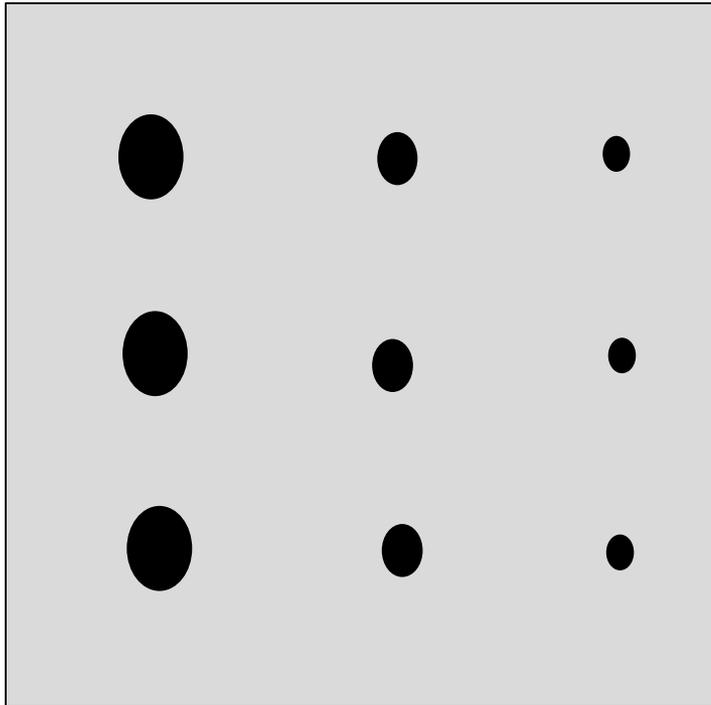
No whisker/hillocks nucleation from grains without oxide
- **Weak oxide is not sufficient to form whisker**

Nucleation not due to grains with weaker oxide layer

- Sputtered off oxide using FIB
  - 3 *3 array of holes of size .5,2 and 5 micron

No whisker/hillocks nucleation from grains without oxide
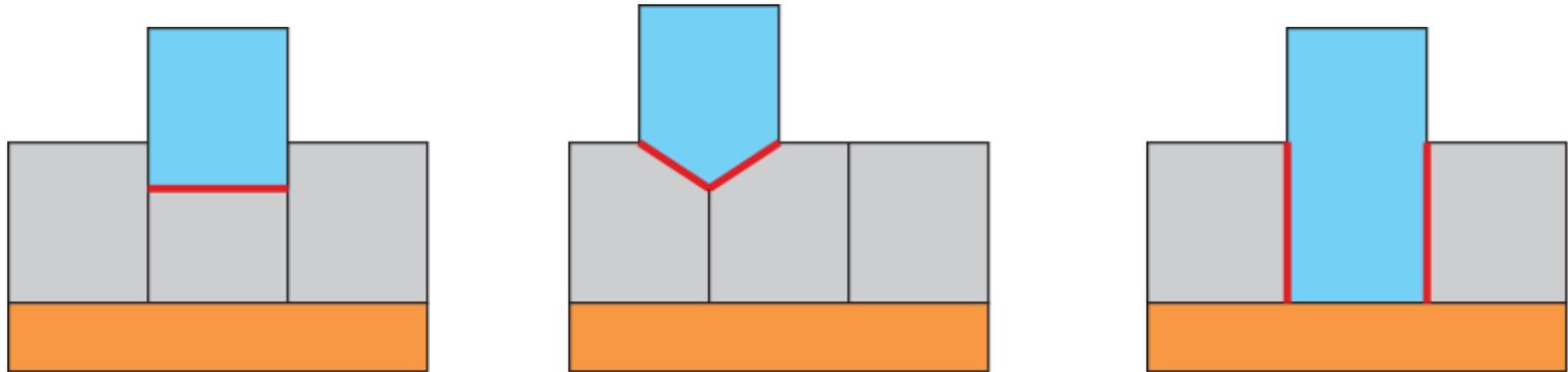- **Weak oxide is not sufficient to form whisker**

Mechanism for whisker nucleation/growth

Enhanced stress relaxation at specific grains ("weak" grains)

<u>Non-columnar grains</u>
e.g., horizontal grain boundaries (Smetana)
Dynamic recrystallization
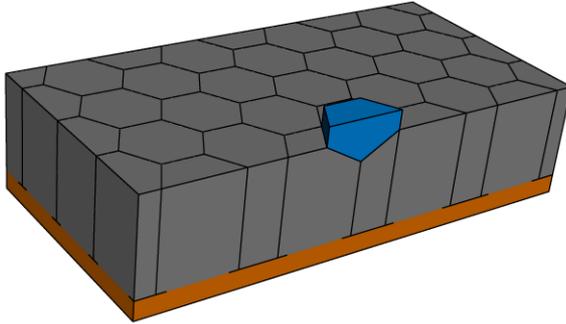
<u>Plastically weak grain</u>
Low yield stress

→ **Maintains low stress at boundary of weak grain**
→ **Creates stress gradient**
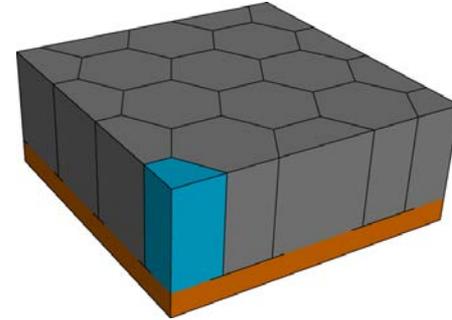   **- induces diffusion through g.b. network**

Add "weak" grain to FEA model to allow whisker growth

- **Different mechanisms to maintain low stress at whisker:**

Shallow whisker root with oblique grain boundaries.

**Whisker with lower yield stress than other grains.**

- **Model IMC growth as uniform volume strain throughout Sn (IMC growth generates *excess* volume in Sn).**

<u>Use FEA to calculate:</u>

- **Stress field that develops around whisker grain.**

- **Rate of material transport to the whisker root (upper limit on whisker growth rate).**

- **Variables are IMC growth rate & whisker spacing.**
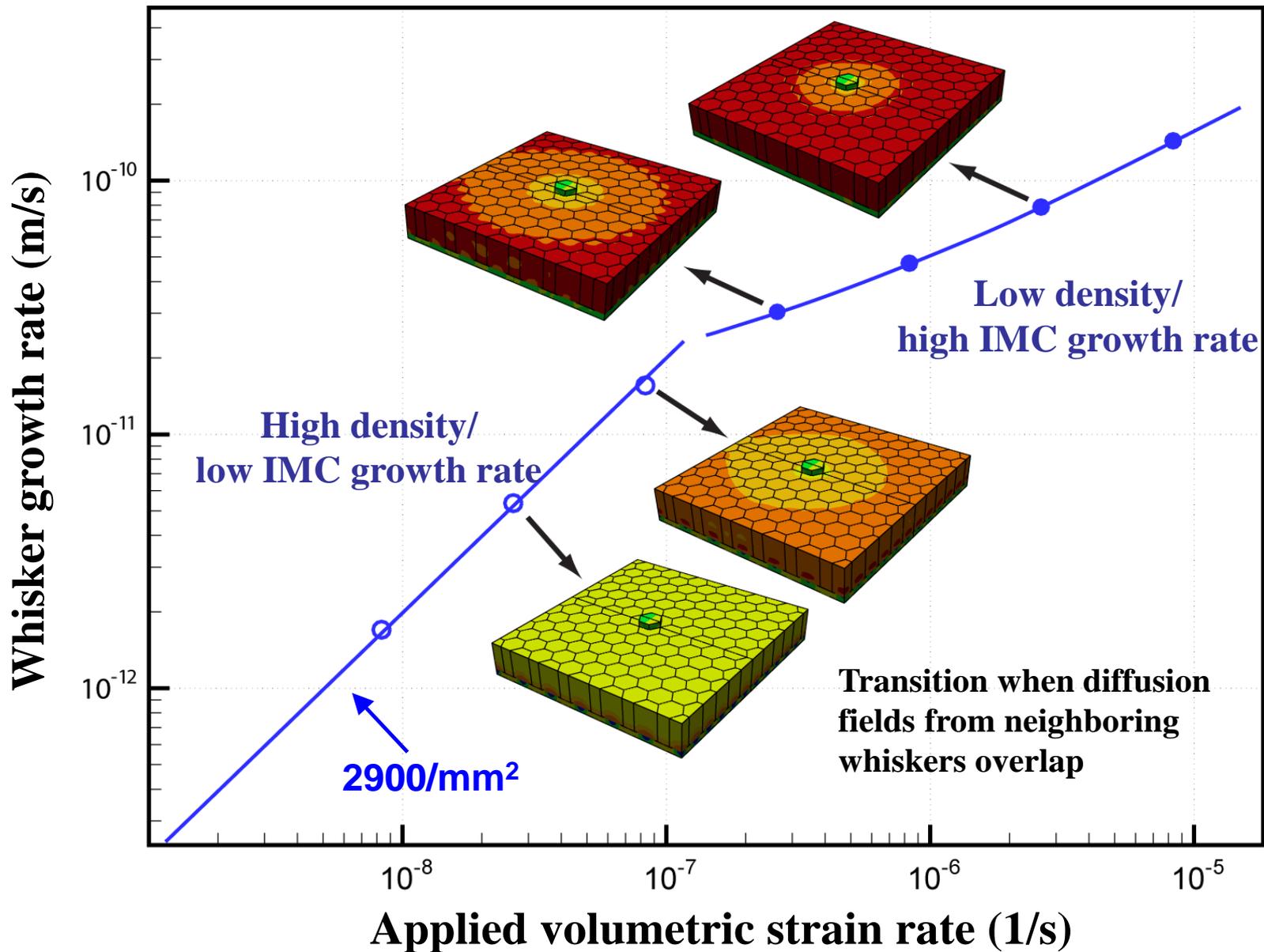
Stress evolution with whisker growth

Large portion of film is at yield stress
(not relaxed by the whisker)

Biaxial
Stress
[MPa]
10
5
0
-5
-10
-15
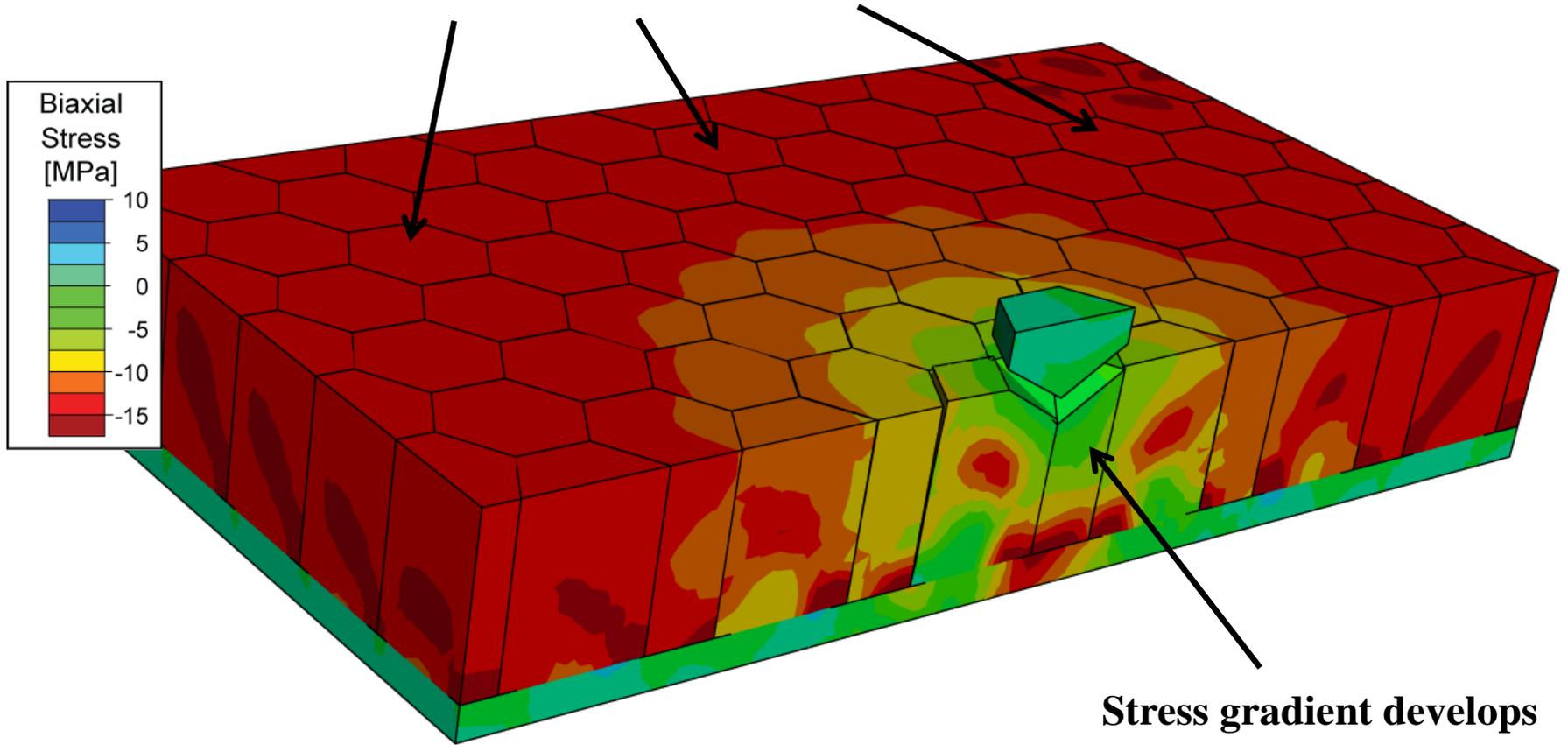
**Stress gradient develops
radially and vertically
around the whisker root**

(Buchovecky and Bower, APL, 2008)
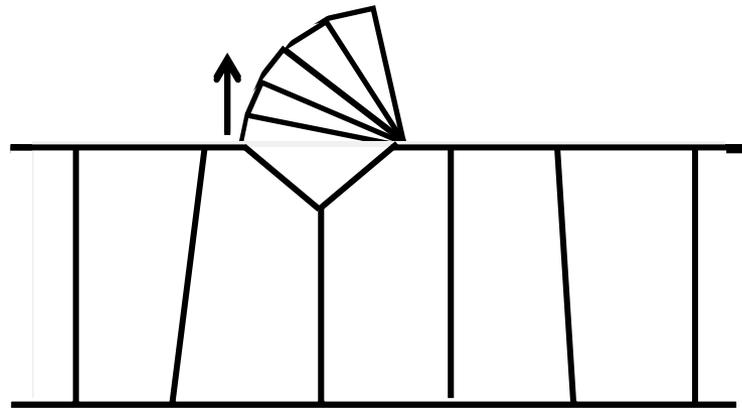
Whisker vs. IMC growth rate from FEA models

Whisker growth rate (m/s) (y-axis)

Applied volumetric strain rate (1/s) (x-axis)

Low density/
high IMC growth rate

High density/
low IMC growth rate

2900/mm²

Transition when diffusion
fields from neighboring
whiskers overlap

Other observations of surface evolution
Not only whiskers grow

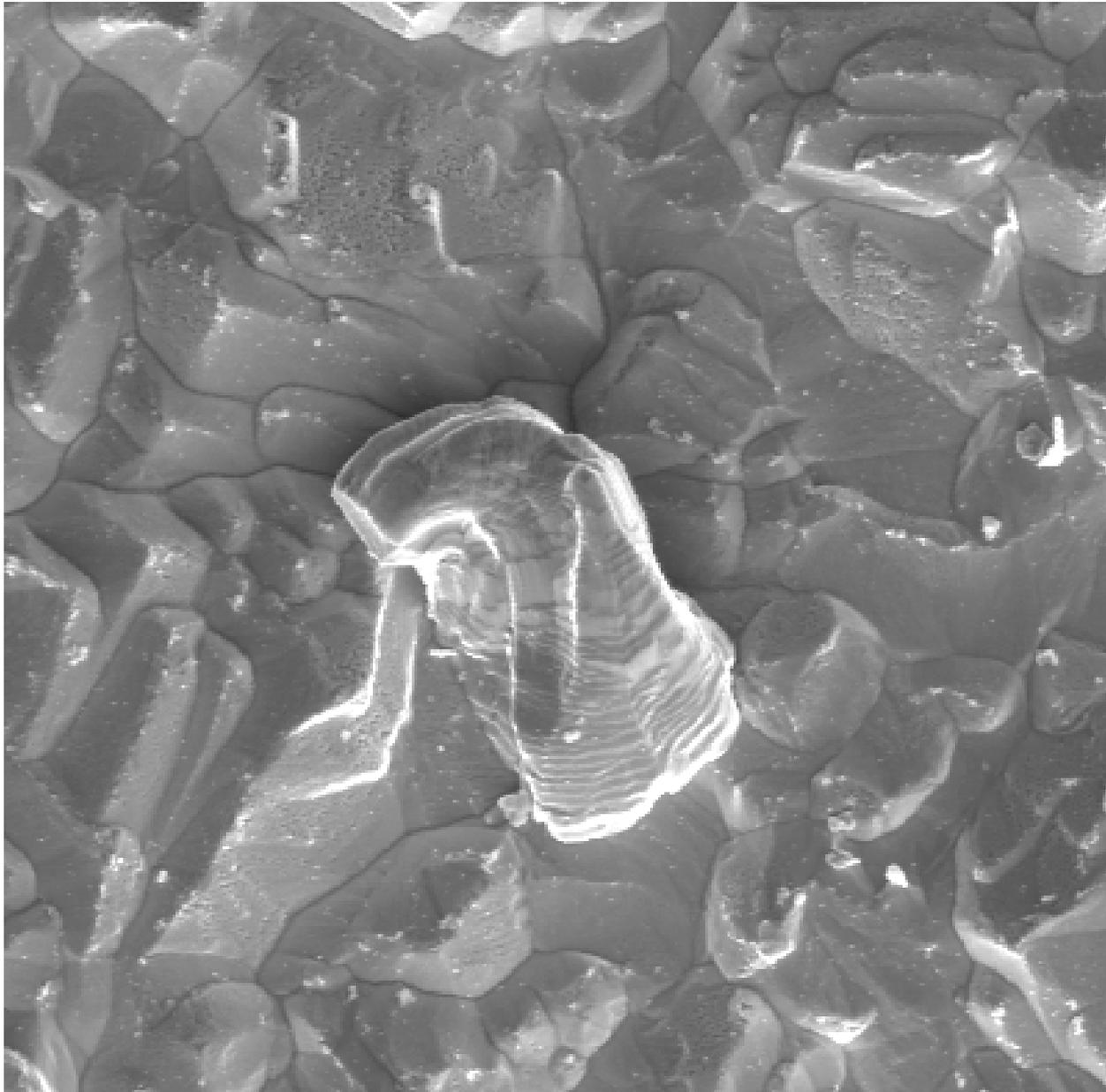**Movie #5**

2 µm
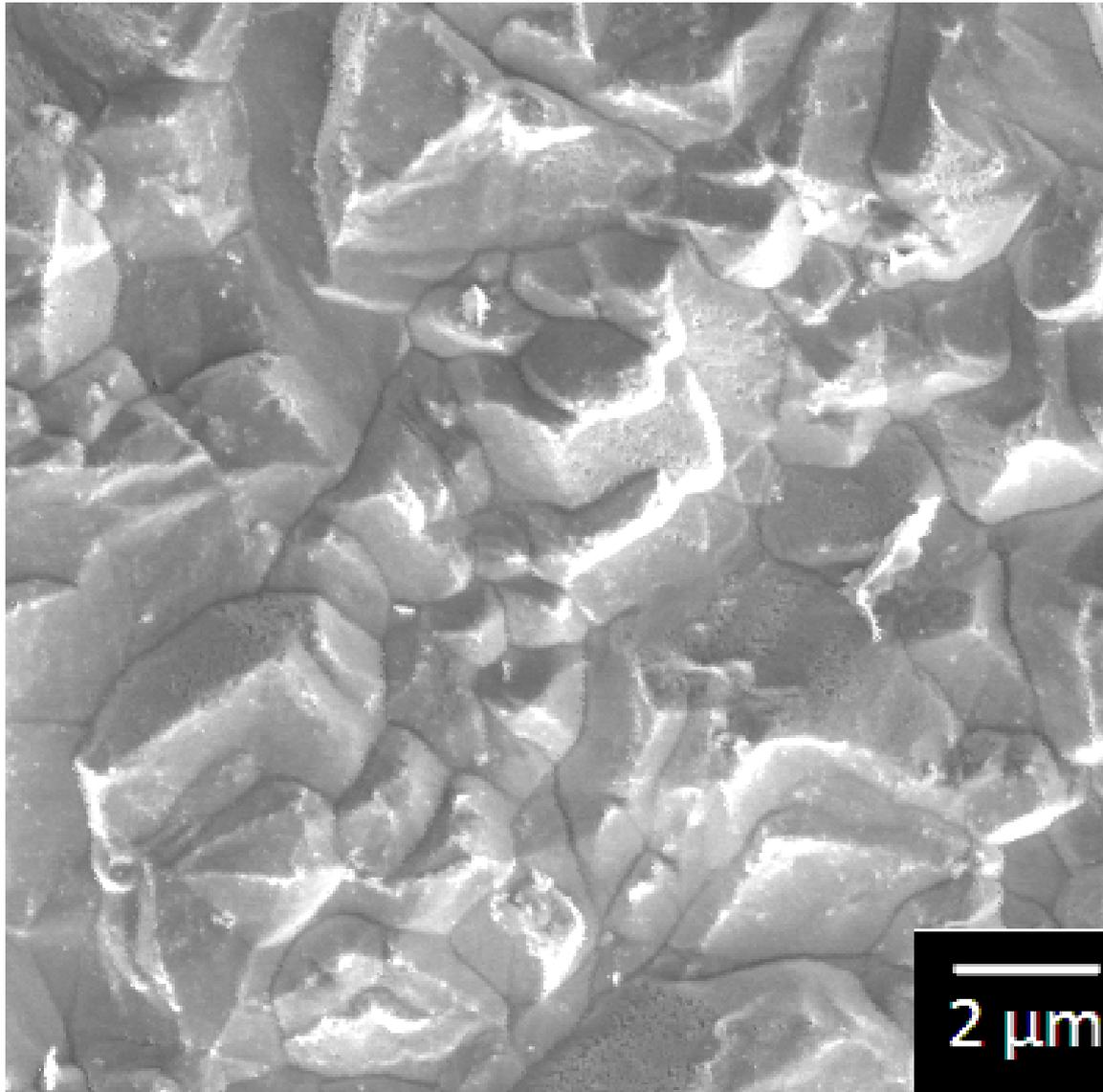
Schematic Explanation
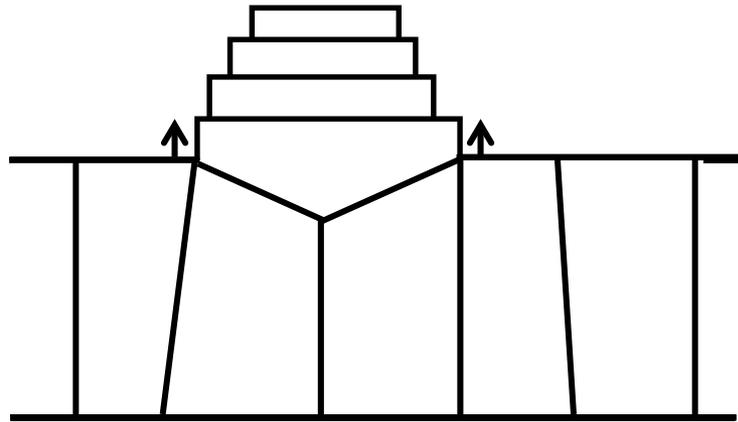

Tilt

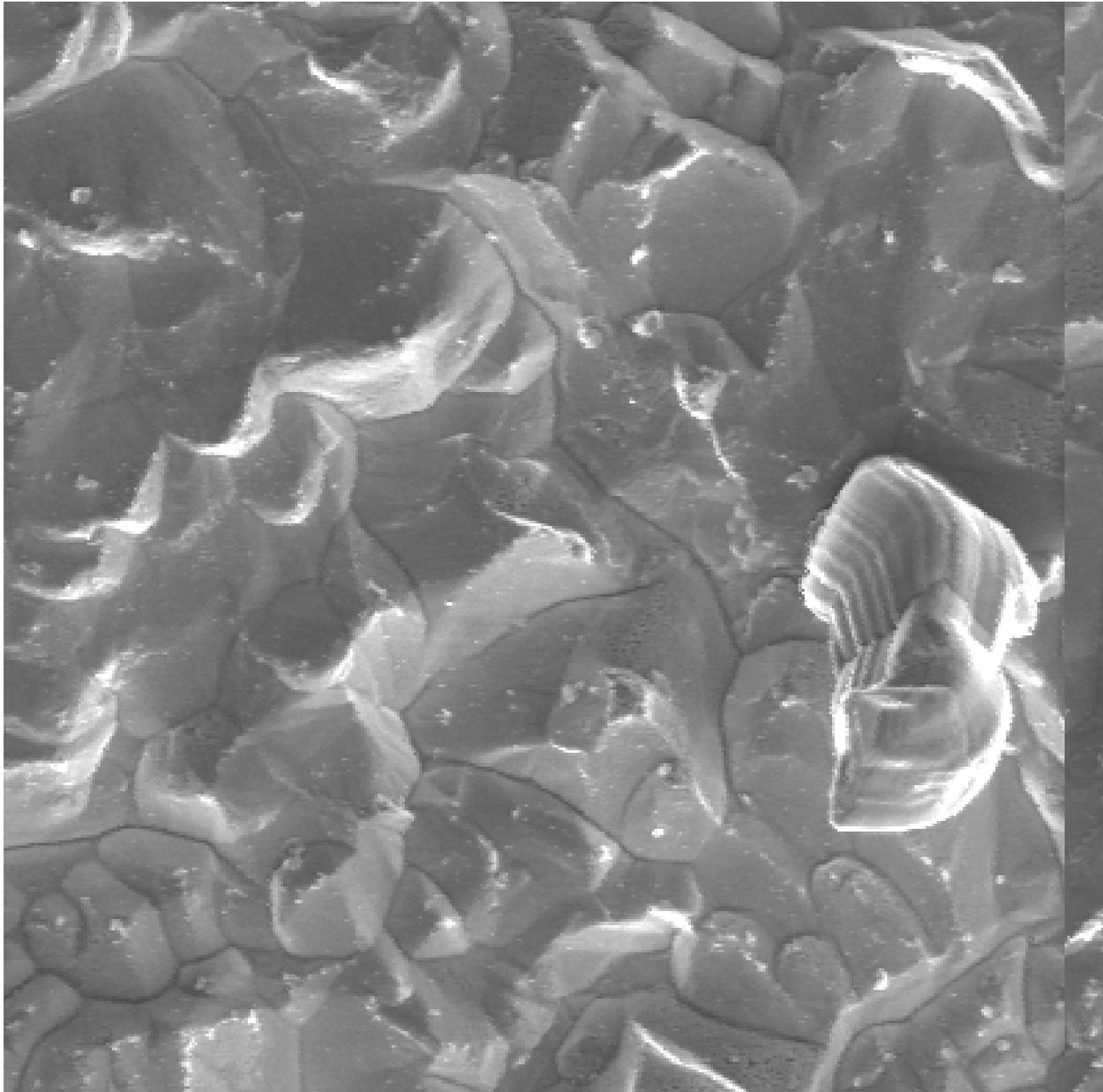# What determine the hillocks shape ?

Movie #2

2 μm

Schematic Explanation

Hillocks nucleation and growth from partial grain
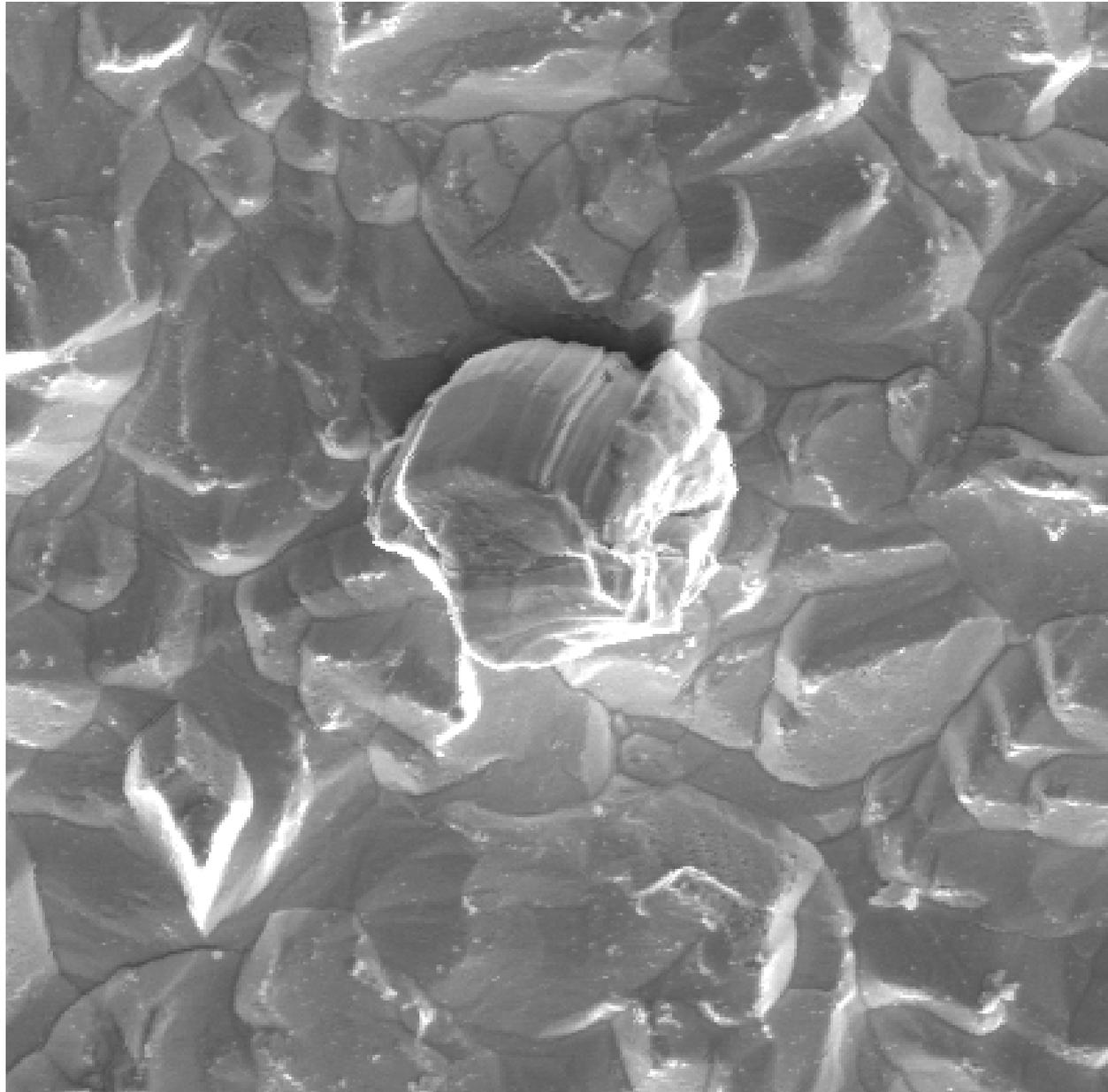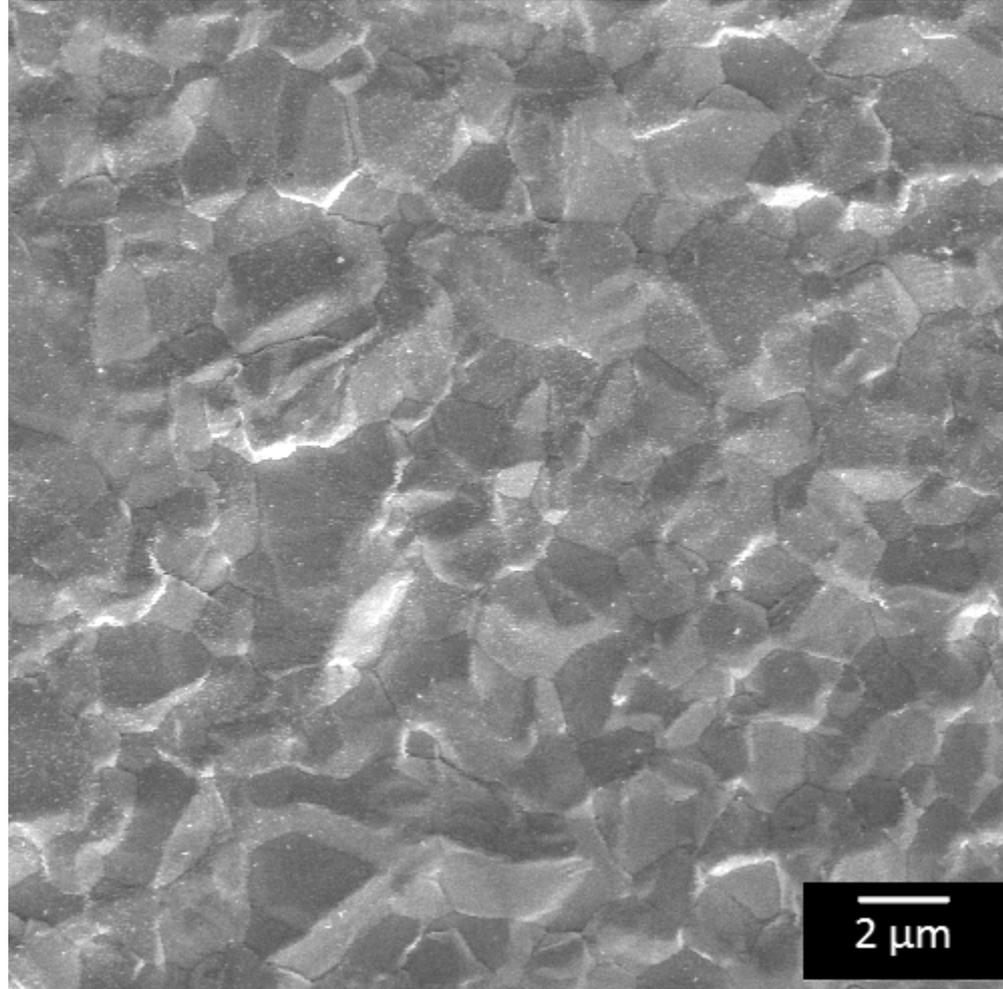
Movie #3

2 μm

Grain growth then hillock pops out
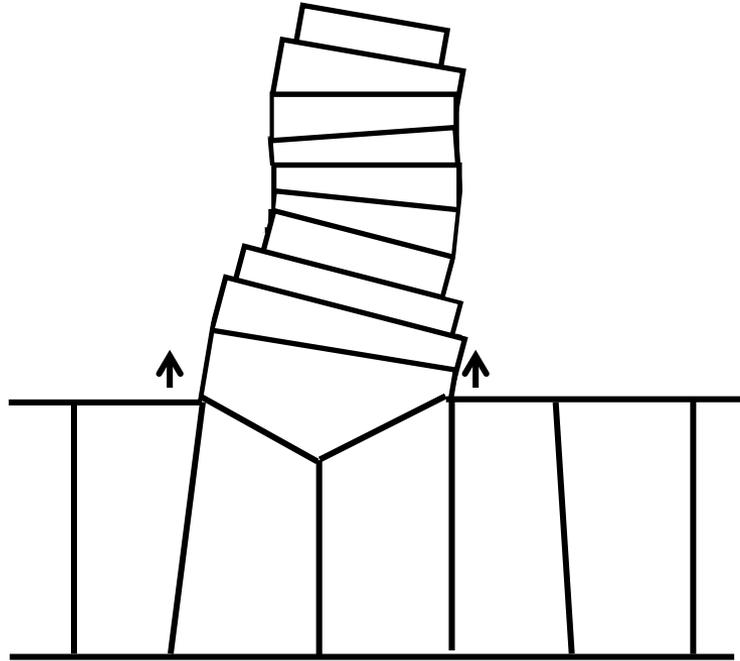
Movie #4

2 µm

Grain Growth w/o hillock

2 μm

Schematic Explanation

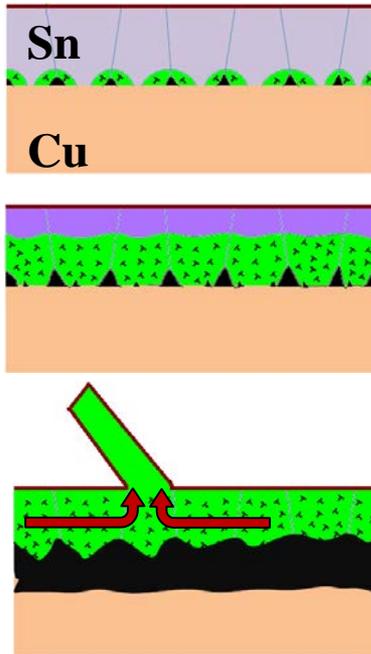## Complex morphologies

Combination of

- Vertical Growth

- Lateral (Grain) Growth

- Tilt

Future

Model with FEA

- Non-uniform stress

- Non-uniform mass flow

- Grain growth

Summary - Mechanisms of whisker growth

1) Cu diffuses into Sn to form IMC
2) IMC grows → stress spreads through Sn
    - *dislocation motion/point defects*
3) Oxide prevents defect annihilation at surface
    – *stress builds up in layer*
4) Stress causes yield of "weak" grain
    – *allows whisker to grow*
5) Stress gradient drives diffusion to whisker base

Suggestions for mitigation

- Enhance stress relaxation in Sn
    • *don't strengthen Sn!*
- Modify microstructure of Sn or IMC to reduce stress
    • *promote horizontal GB's as sinks (like Pb)*
- Weaken oxide
    • *enhance stress relaxation at top surface*
- Diffusion barriers
    • *these don't stop driving force for whisker formation*

Thanks to my collaborators:

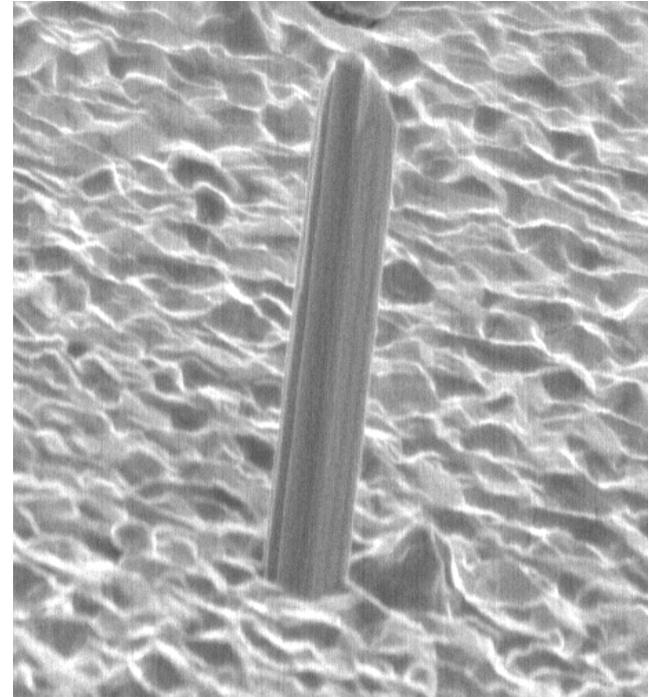Brown: EMC:
Sharvan Kumar   Gordon Barr
Allan Bower
Nitin Jadhav
Eric Buchovecky
Jae Wook Shin (NIST)
Lucine Reinbold (Raytheon)

NSF-MREC AND NSF-DMR for support