Sn whisker formation: relationship between intermetallic formation, stress and whisker nucleation

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EMC:

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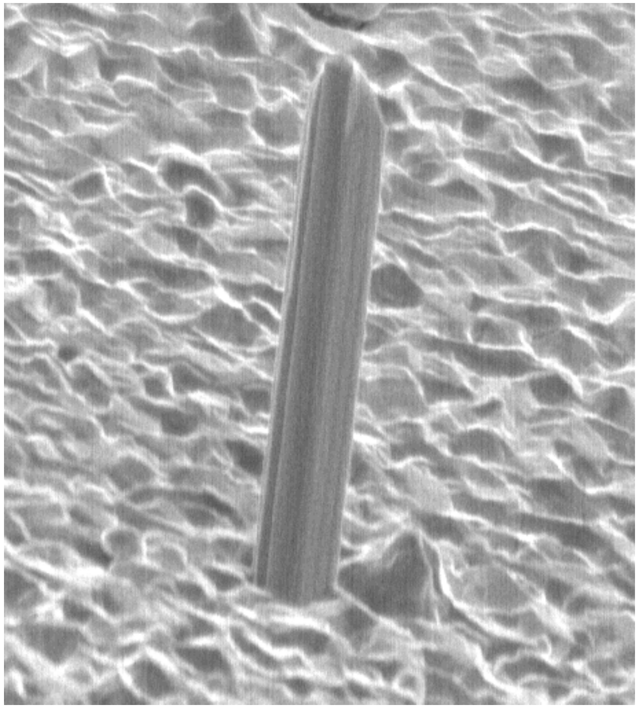
Support:

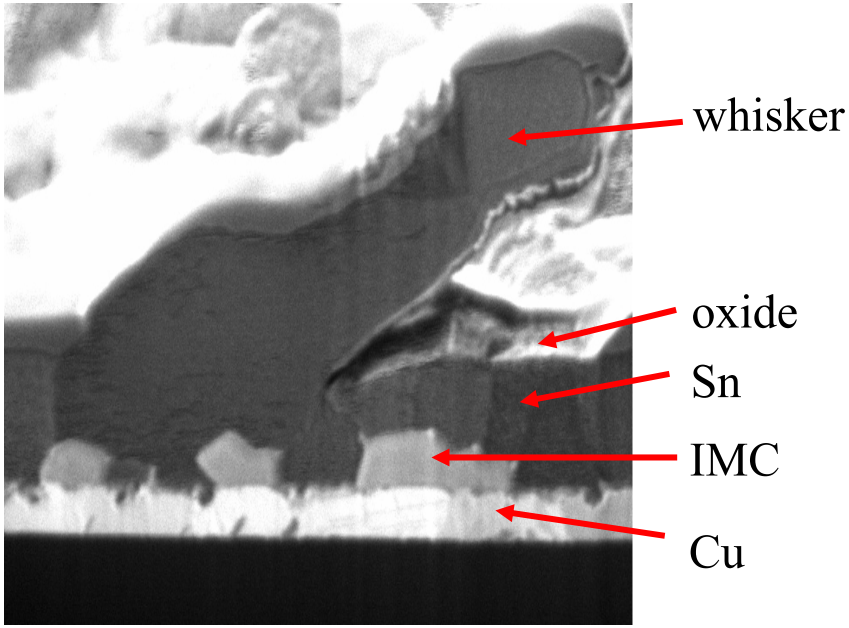
- NSF/MRSEC
- NSF/DMR
- EMC Corp.



Why and how do whiskers form in Sn films on Cu layers?

Problem: Pure Sn forms whiskers on Cu

- **Failures in satellites, pacemakers, missiles (http://nepp.nasa.gov/whisker)**
- **Difficulty: multiple materials processes control whisker formation**



- Complex multilayer structure with multiple phases

- Sn, Cu, IMC, oxide

- Many kinetic processes to consider:

- deposition processes
- microstructural evolution
- interdiffusion of Cu/Sn
- intermetallic growth
- stress generation in Sn
- whisker nucleation and growth

Lots of prior and ongoing work

- many different systems/processing methods
- samples often not fully characterized
- need systematic studies to identify mechanisms/develop models

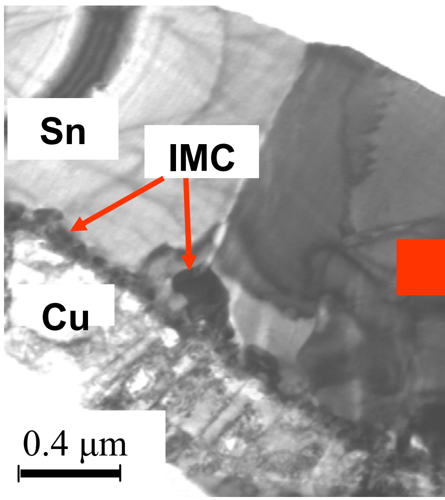
Focus: How are IMC growth, stress and whisker formation connected?

- How does IMC growth lead to stress?

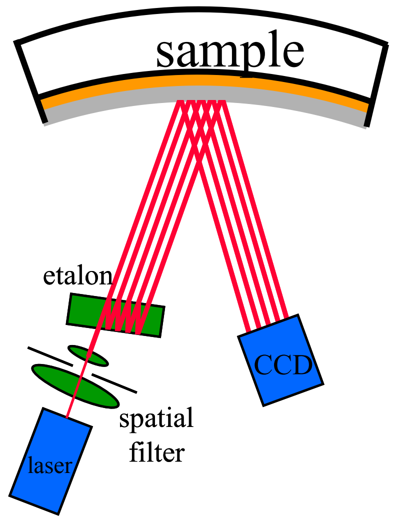
- How does stress lead to whiskers?

- How does Pb suppress whisker growth?

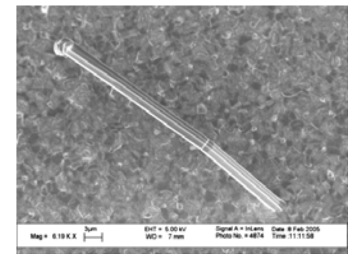
IMC

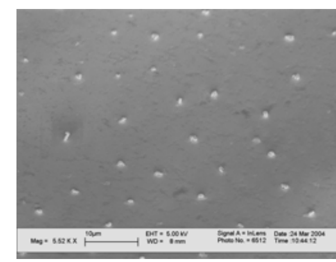


stress



whiskers





Approach:

1) Simultaneously measure kinetic evolution of

IMC, stress, whisker density

2) Microscopic measurements of mechanisms (*TEM*)

3) Develop picture of processes controlling whiskers (*FEA models*)

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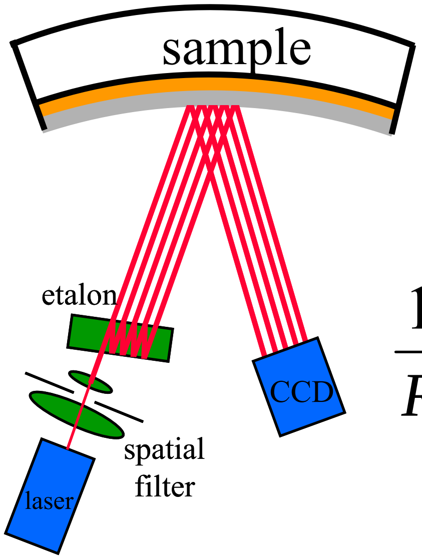
Measure stress evolution using wafer curvature



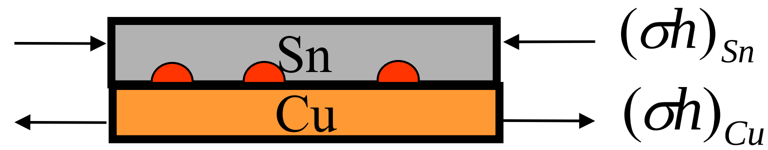
MOSS (Multi-beam Optical Stress Sensor)

$$\frac{1}{R} = \frac{6}{M_s h_s^2} \sum_i \langle \sigma_i \rangle h_i$$

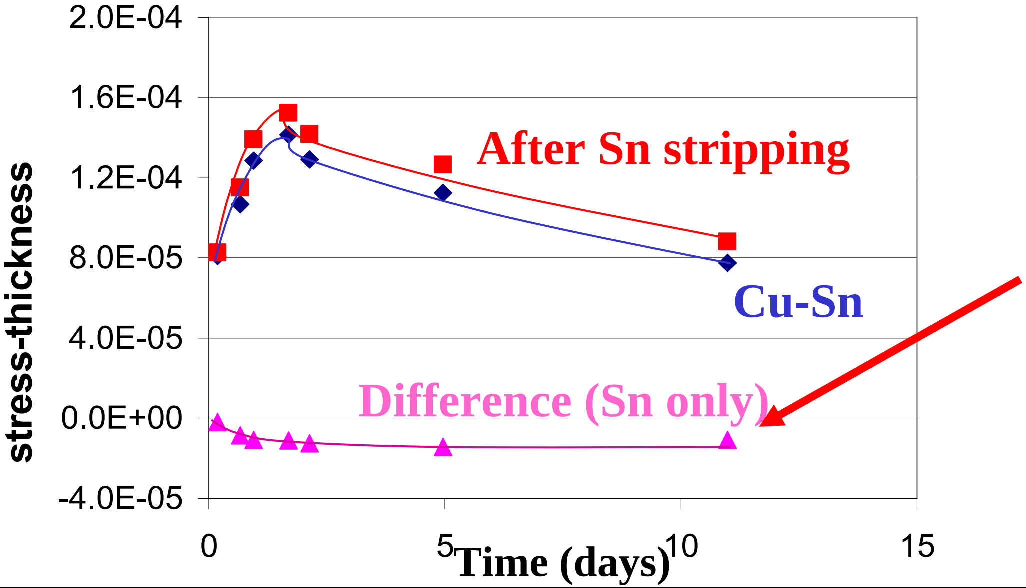
i=Sn, Cu, IMC

Difficulty:

Measurement is sum of <σh> in multiple layers (Cu, Sn, IMC)



Measure stress in Sn separately by removing layer chemically



Remove Sn layer by etching – Measure change in curvature

Difference due to stress in Sn only!

Sn stress saturates at appr. 10 - 15 MPa

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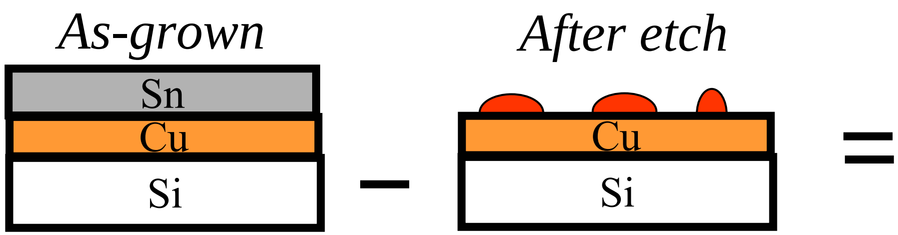
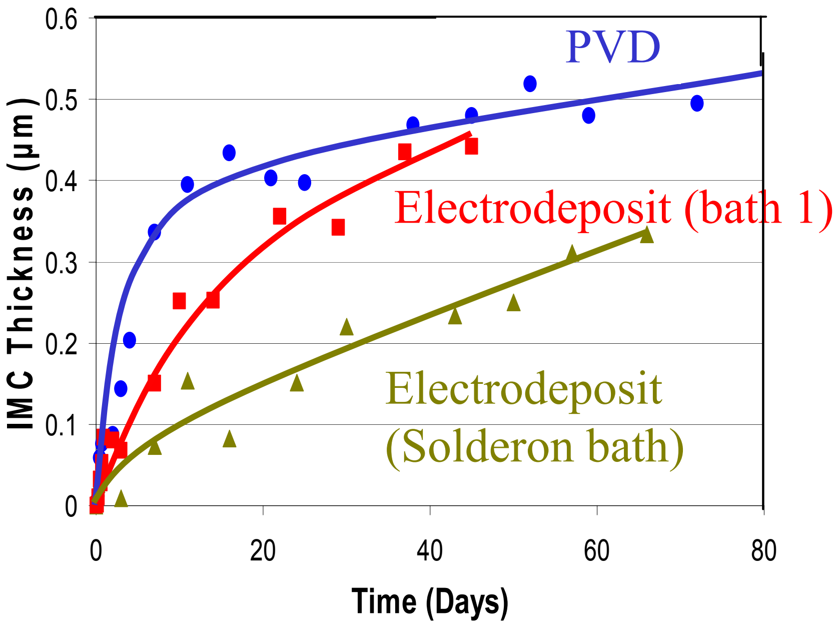
Measure intermetallic volume to relate to stress

Methods: weight change after Sn stripped off; X-ray diffraction of IMC peaks



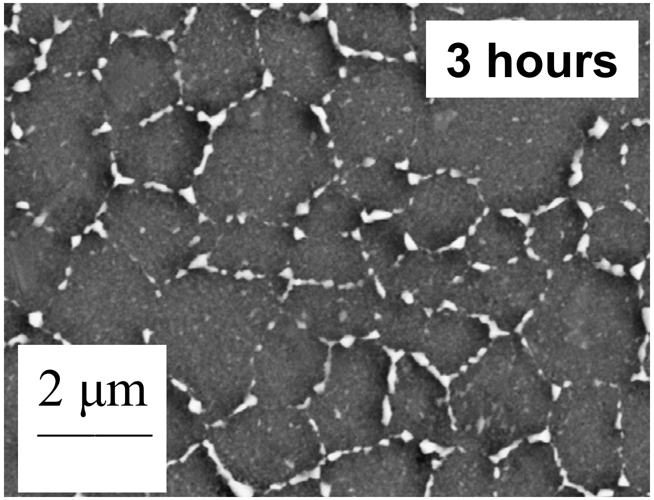
Mass of un-reacted Sn

IMC growth kinetics



May depend on deposition process

Electroplated



Nucleation at Sn-Sn grain boundaries at Cu-Sn interface

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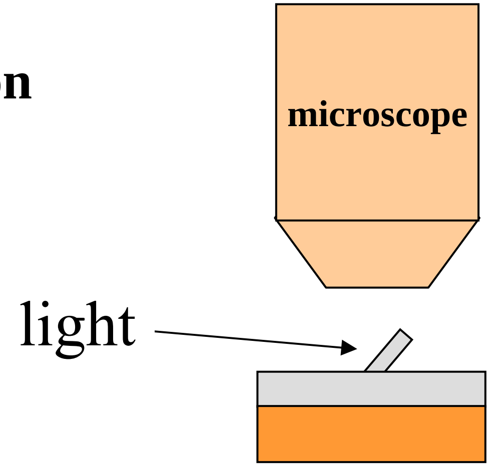
Measure whisker density using optical microscopy

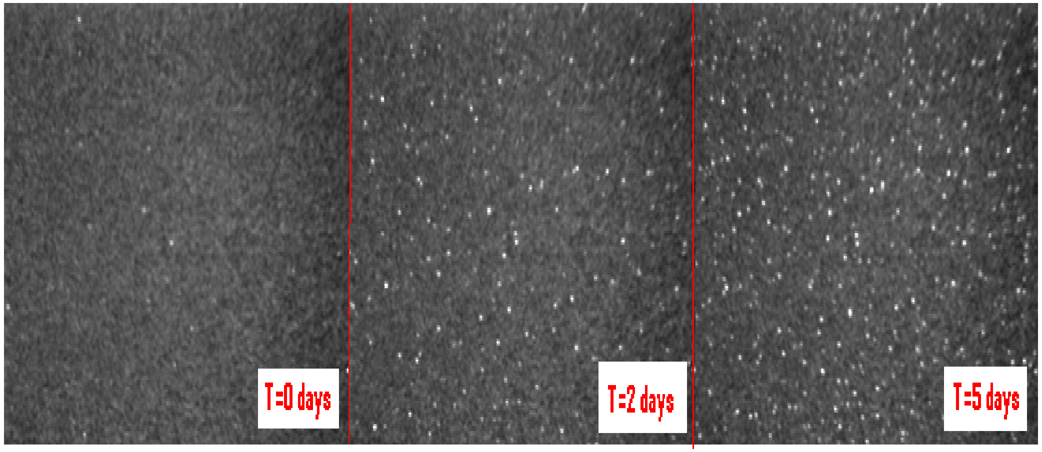
Have to measure small features/large field of view

Optical microscopy with oblique illumination enhances scattered light from whisker

Real-time monitor of whisker density



Quantify density from optical images



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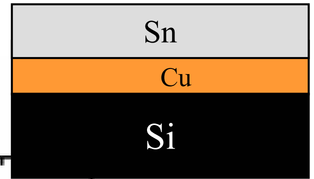
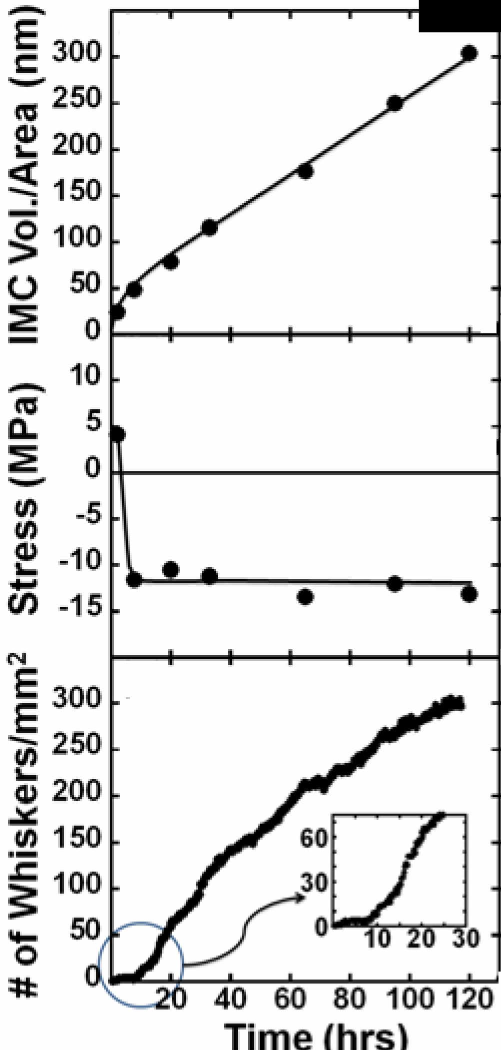
Correlate stress/whiskering with IMC growth

Chason APL 2008

Pure Sn on Cu



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)

- Whiskers start to grow after stress saturates

-Stress saturation may not be due to whiskering

→ Also onset of plastic deformation

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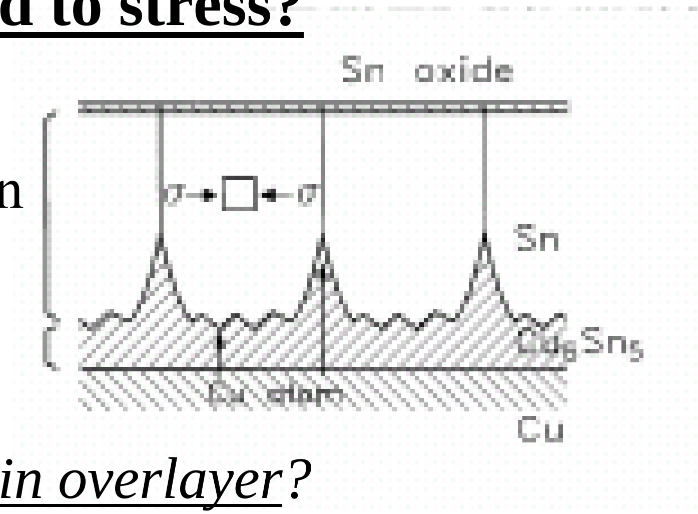
How does IMC growth lead to stress?

"Standard picture": IMC grows into grain boundary to create stress in Sn layer (Lee and Lee, Acta Mat, 1998)



<u>How does growth of IMC layer cause stress in overlayer</u>?

- *Volume expansion → strain around growing particles*
- *But must be more than elastic effects:*
  - *elastic stress in buried layer does not necessarily cause stress in overlayer (e.g. thermally generated stress due to CTE mismatch)*
  - *elastic stress fields decay rapidly ($1/r^3$) so small at oxide surface*
  - *stress quickly exceeds yield stress as particles grow*

***Must consider:** - processes of stress generation/relaxation*
- plastic deformation
(dislocation motion, diffusion of atoms/defects)

TEM to study stress generation/relaxation on micro-scale

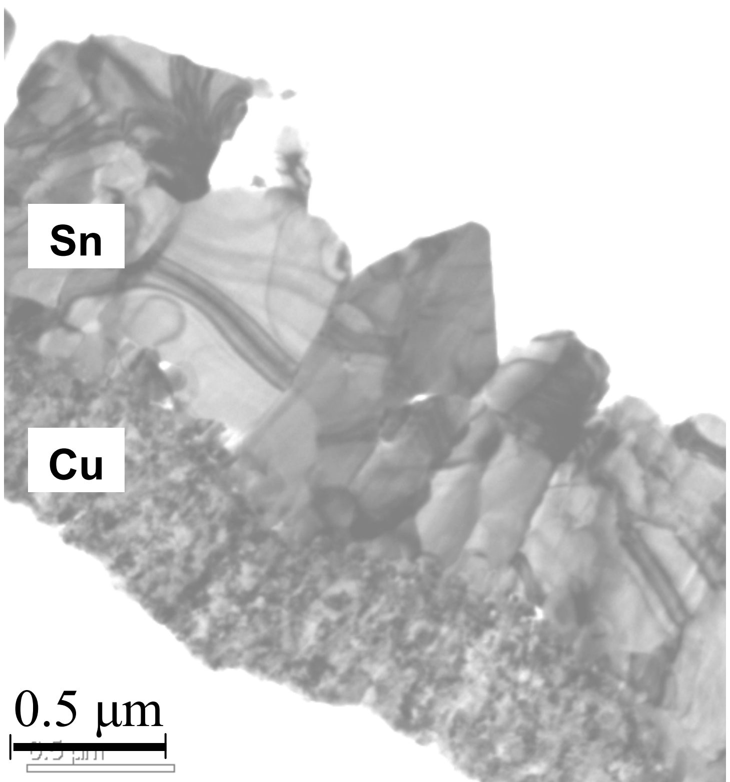
Kumar, JMR 2008

Ultra-Microtomed XTEM samples preserves interface

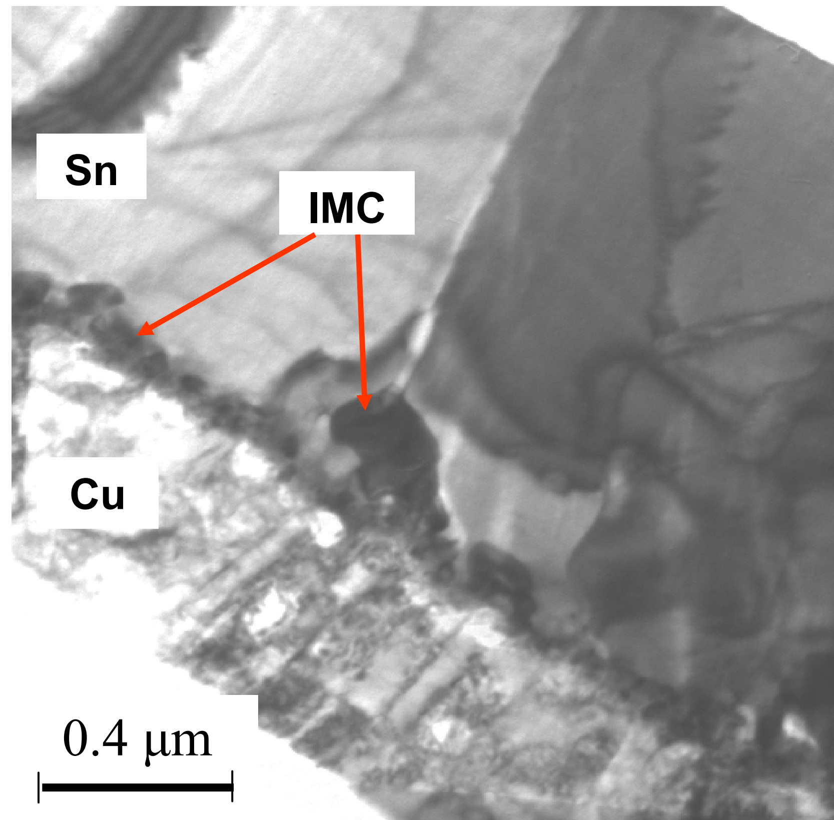
12,000Å Sn/6000Å Cu

Evolution of IMC microstructure

As-prepared

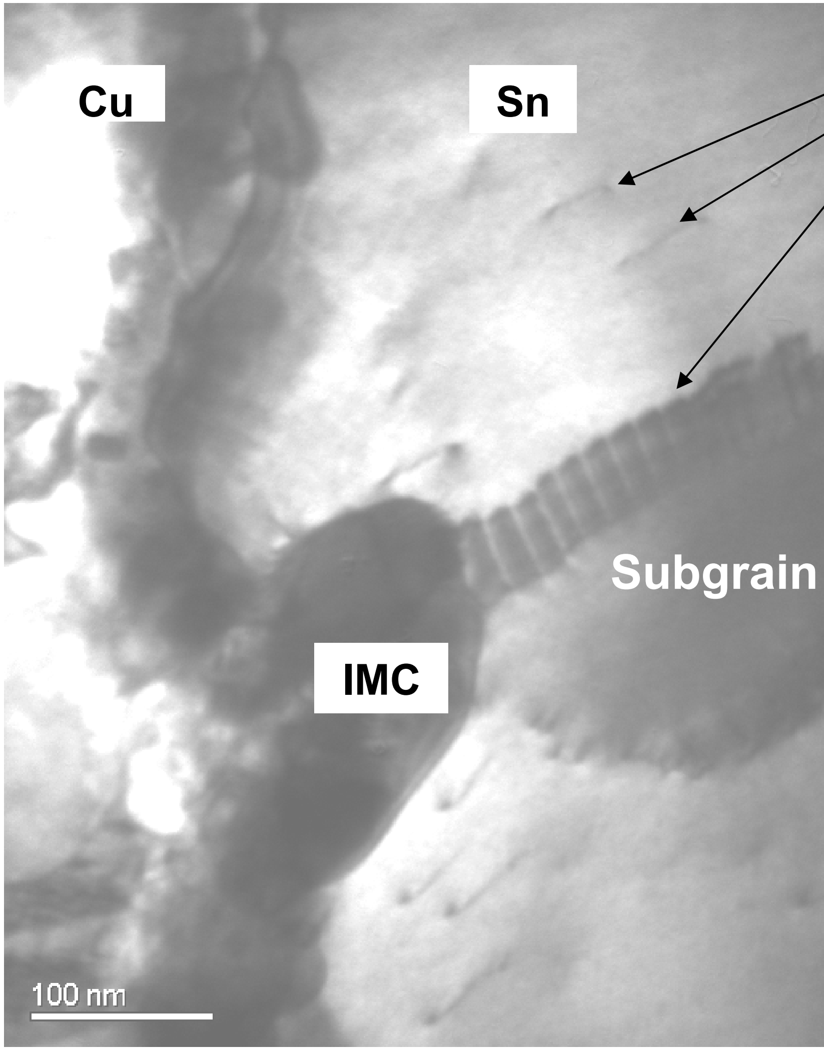


After 5 days (IMC present)



TEM shows stress relaxation by dislocation formation

Cross-Section TEM Samples : 5 Days (12,000Å Sn/6000Å Cu)



Extensive dislocation emission around IMC particles

- *transmits strain into Sn layer*

Dislocations form into subgrain boundaries

Sn at room temperature is at 0.6 T_m

- *large amount of dislocation mobility*

Diffusion of point defects along grain boundaries also occurs

- *not visible in TEM*

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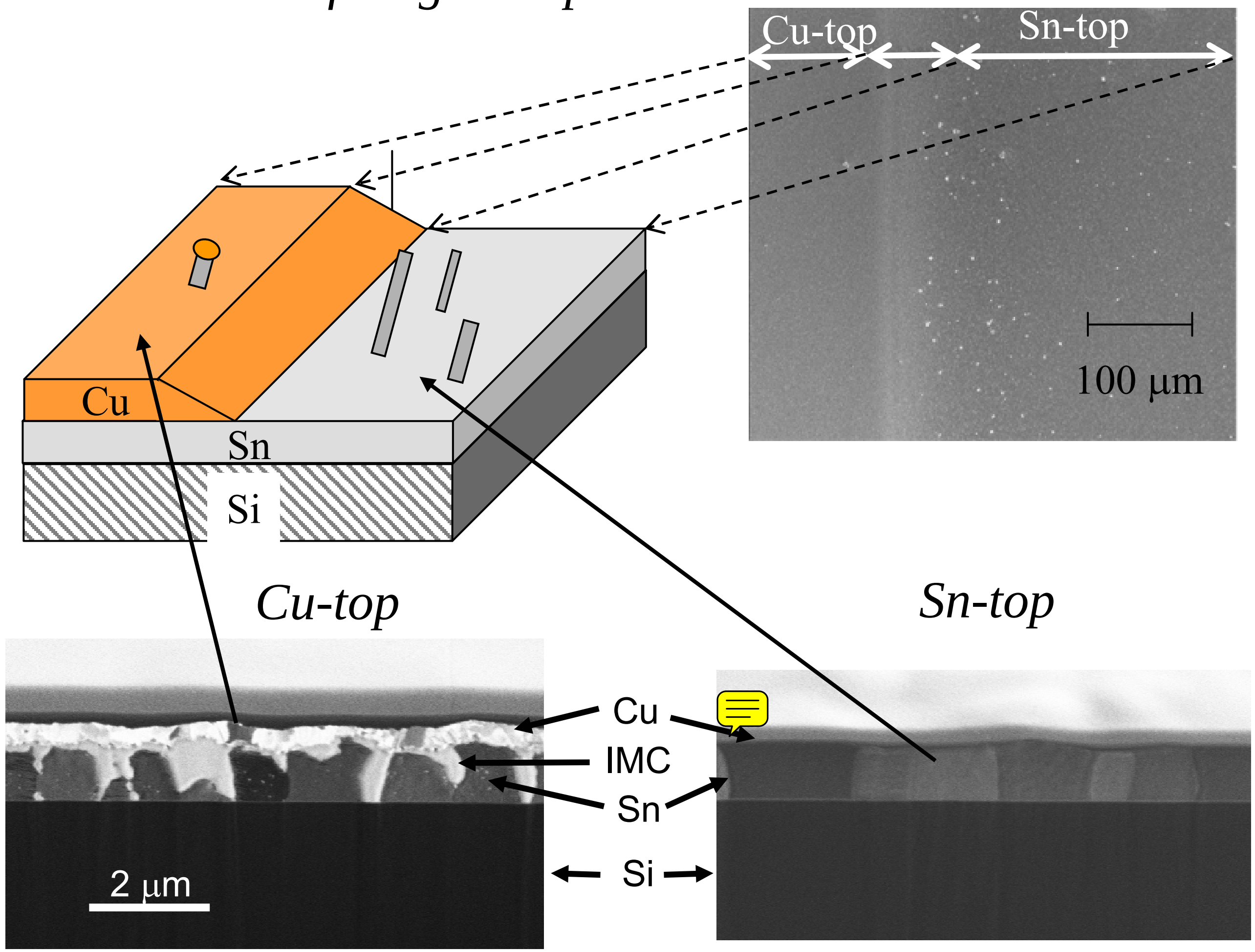
Effect of long range diffusion: quantify with "ledge sample":

Schematic of ledge sample *SEM around ledge*

Reinbold, JMR submitted



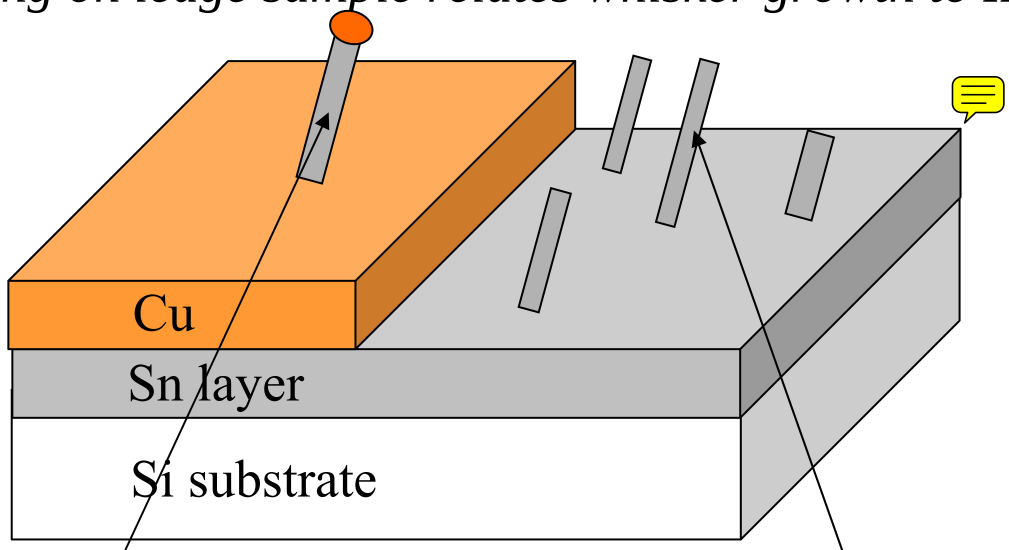
<u>*FIB images of ledge sample*</u> - *No IMC 700 microns from ledge*

<u>Ledge sample</u>

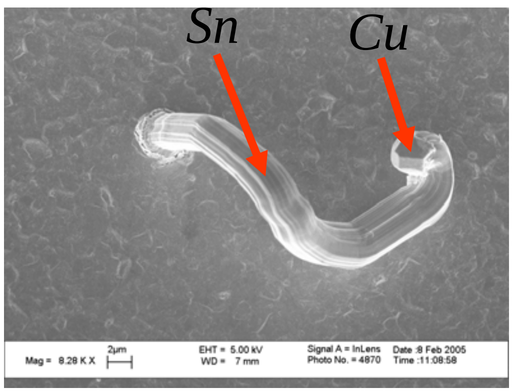
- 1200 nm Sn on Si 600 nm Cu over **half** of Sn layer
- Monitor whisker density with SEM
- Measure Cu evolution with EDS
- Compare evolution of whisker density/ Cu concentration
- FIB shows IMC primarily under Cu *not far out in Sn*

IMC doesn't need to be near whisker

Whiskering on ledge sample relates whisker growth to IMC formation

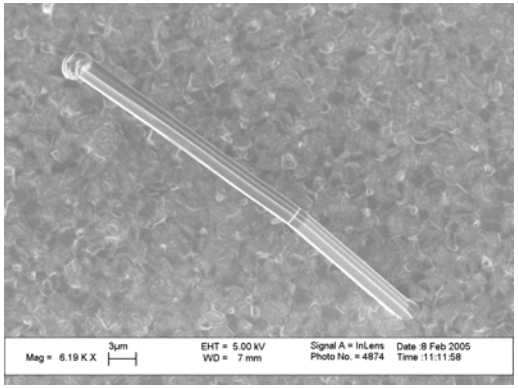


Some whiskers grow through Cu layer



Cu coats tip of whisker

Higher density of whiskers in Sn-top



→no Cu or IMC present

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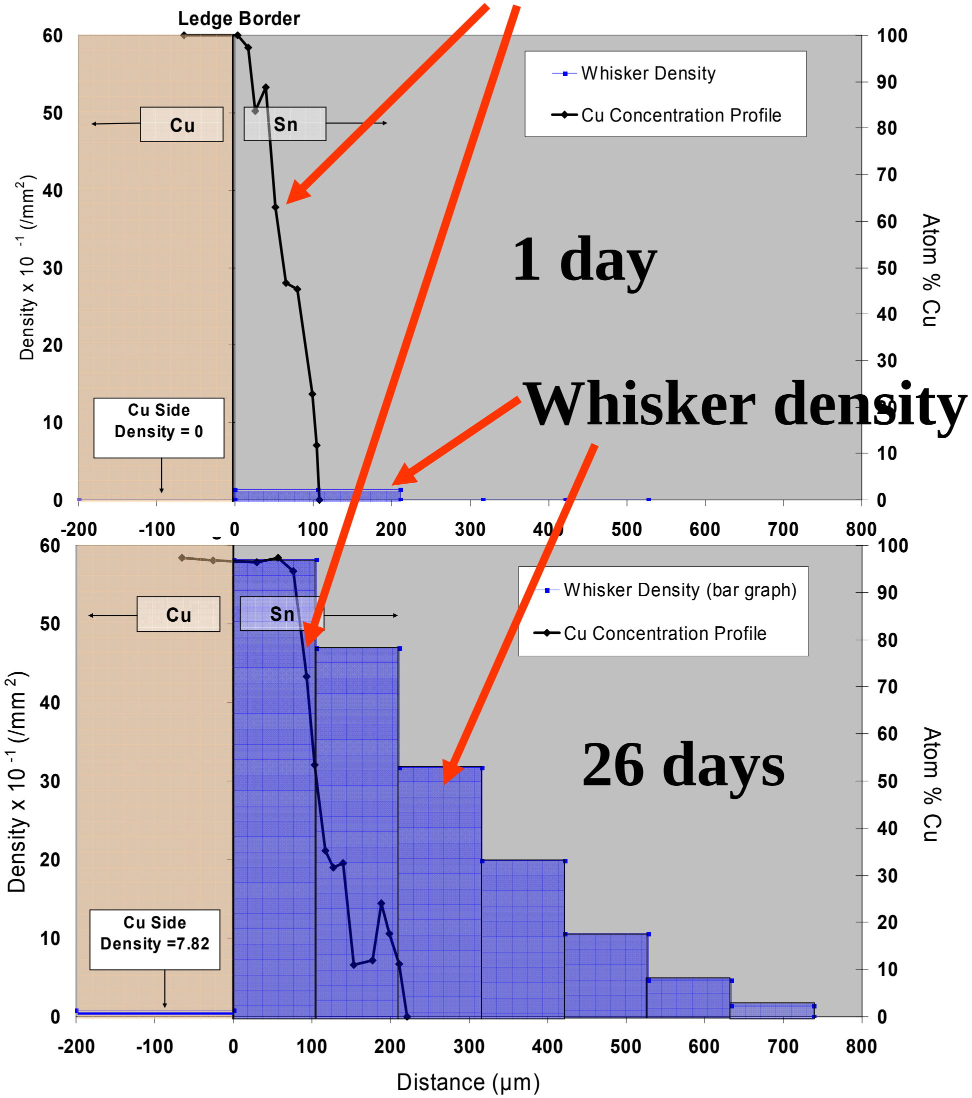
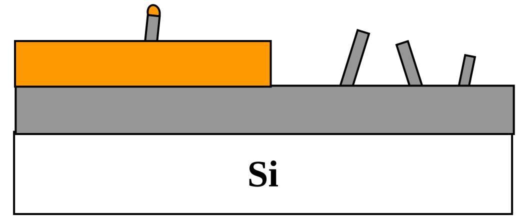
“Ledge sample”: evolution of whisker density/Cu concentration

Cu concentration



distance from Cu edge (micron)



- Monitor whisker density with SEM
- Measure Cu evolution with EDS
- Compare 1 & 26 days

Results

- Cu spreads slowly into Sn
- Whisker density spreads much faster

Consistent with Sn g.b. diffusion

Significance

- Stress spread by long-range Sn diffusion
- IMC not needed where whiskers form

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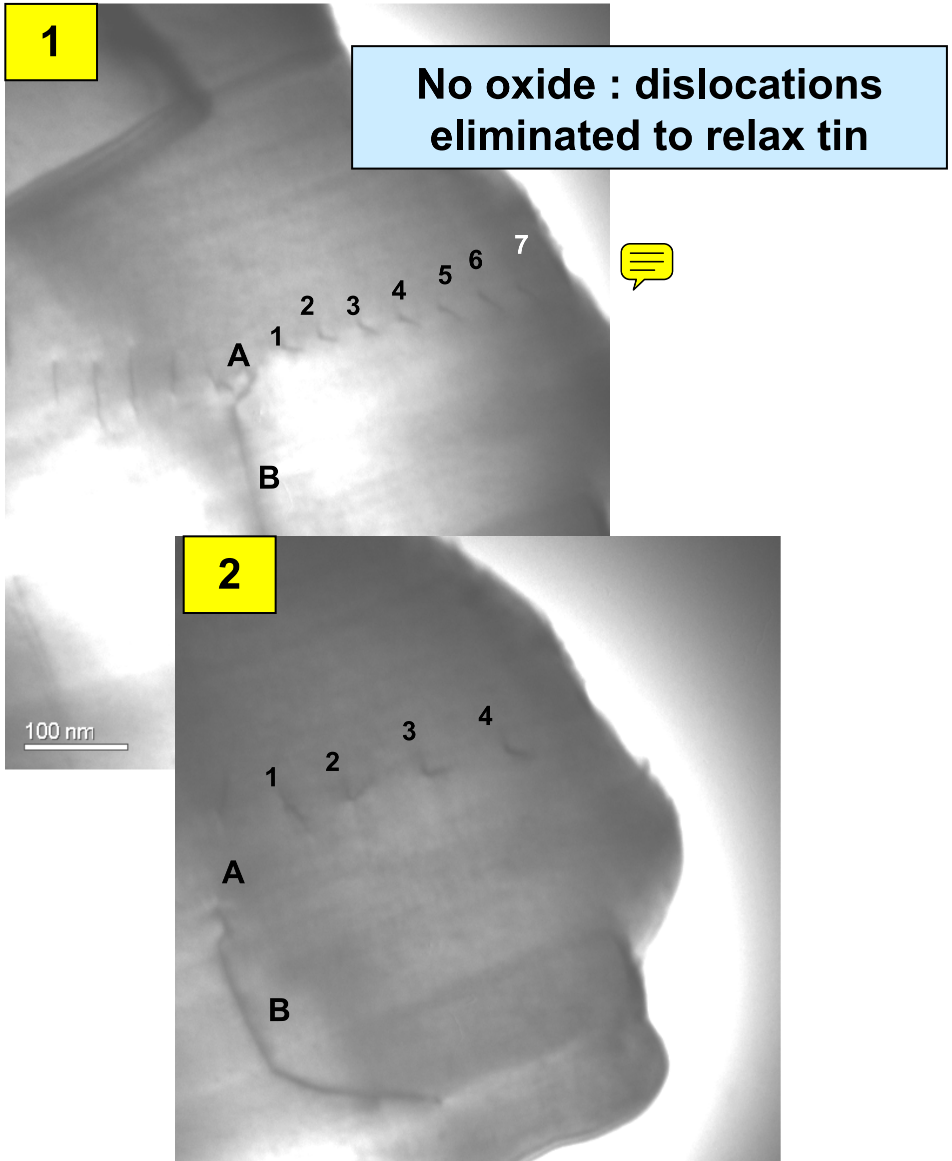
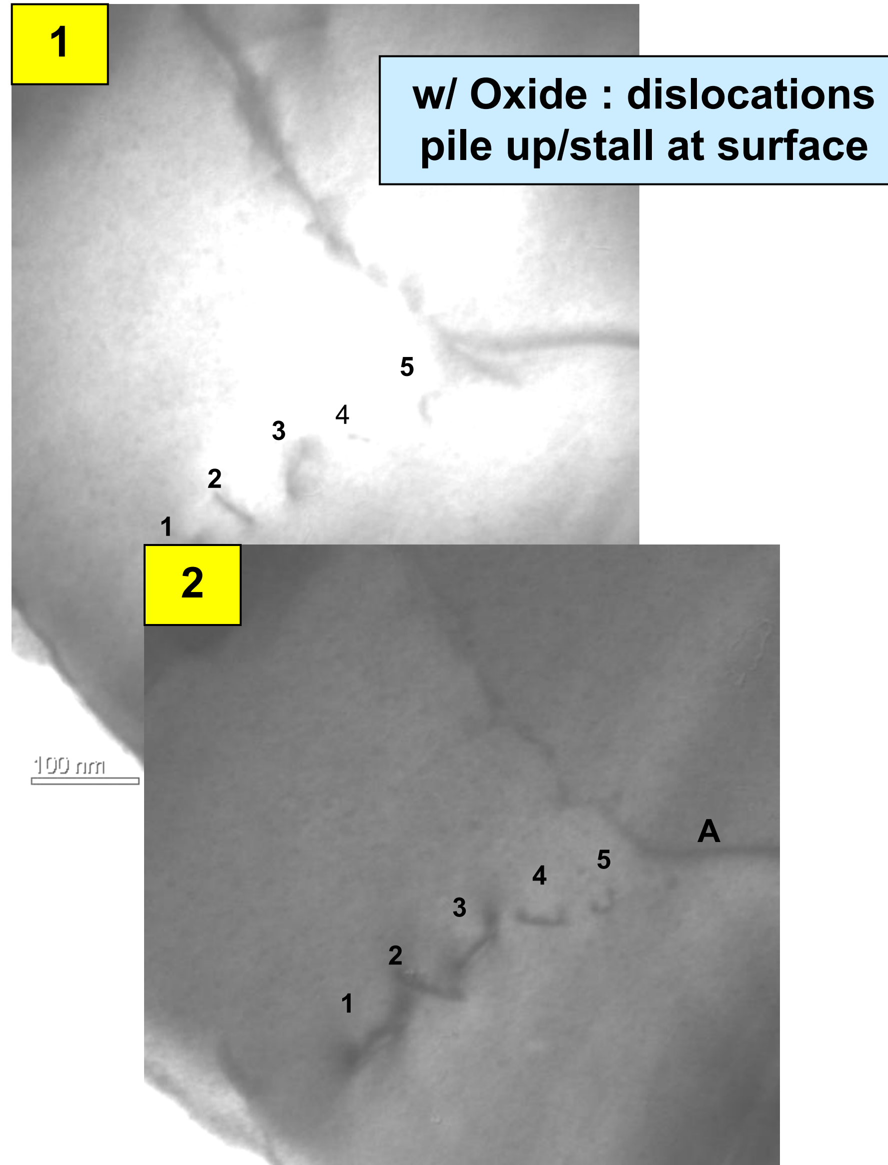
Surface oxide: critical to prevent stress relaxation

Kumar, JMR 2008





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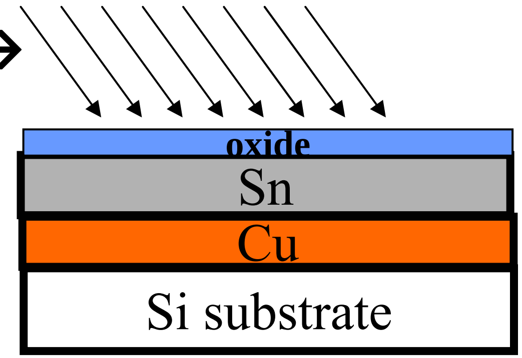
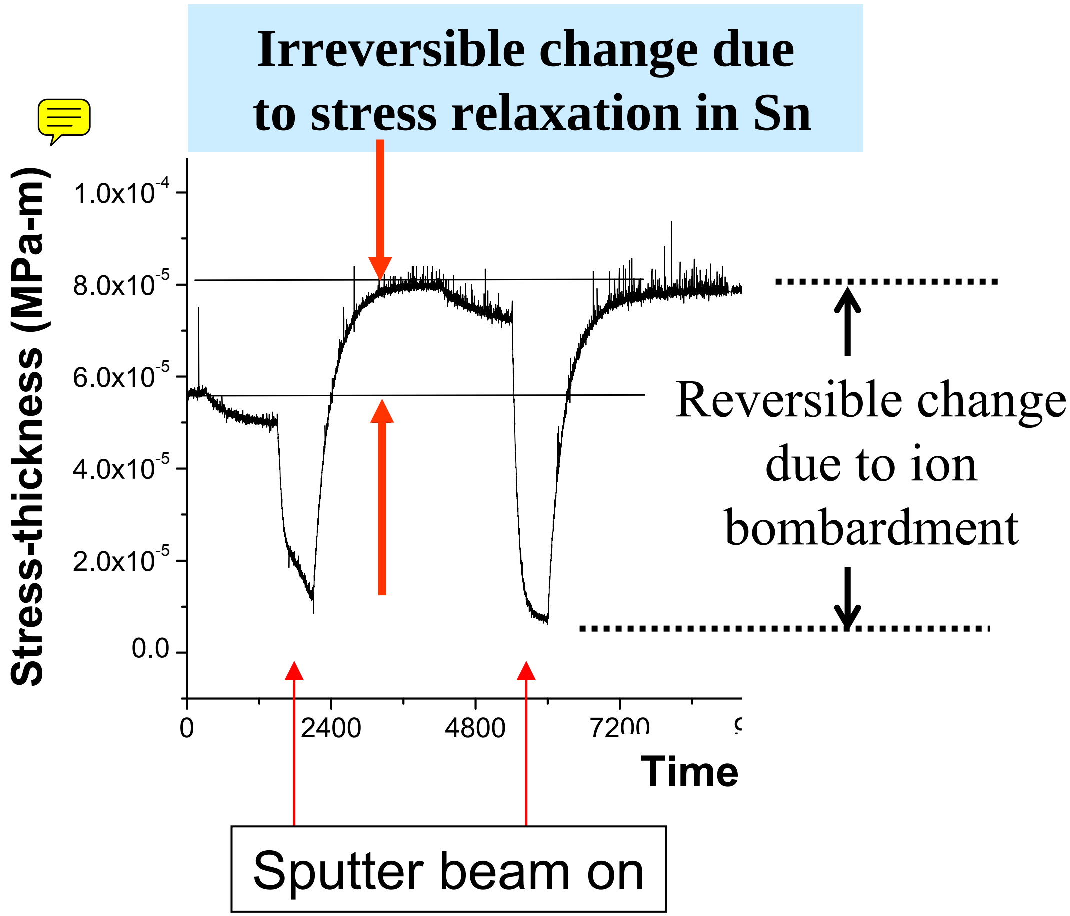
Surface oxide: effect on stress relaxation measured with curvature

Stress relaxes after oxide removed in vacuum — *Chason APL 2008*

Sputter surface in vacuum to remove oxide →





- Removing oxide allows defects to go to surface and relax *compressive* Sn stress:

$\Delta\langle\sigma h\rangle = 2 \times 10^{-5}$ MPa-m

$\Delta\langle\sigma\rangle = 16$ MPa

- Also seen in chemical etching of oxide

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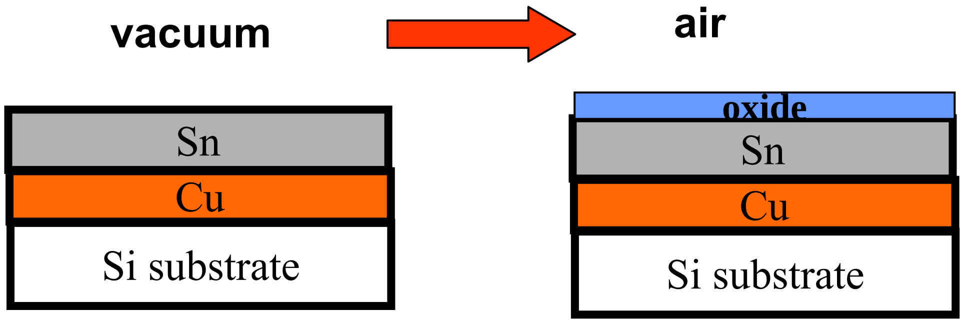
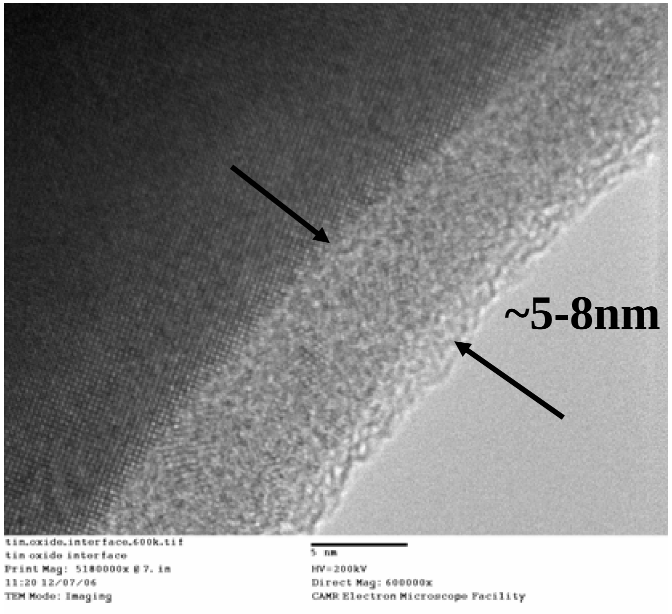
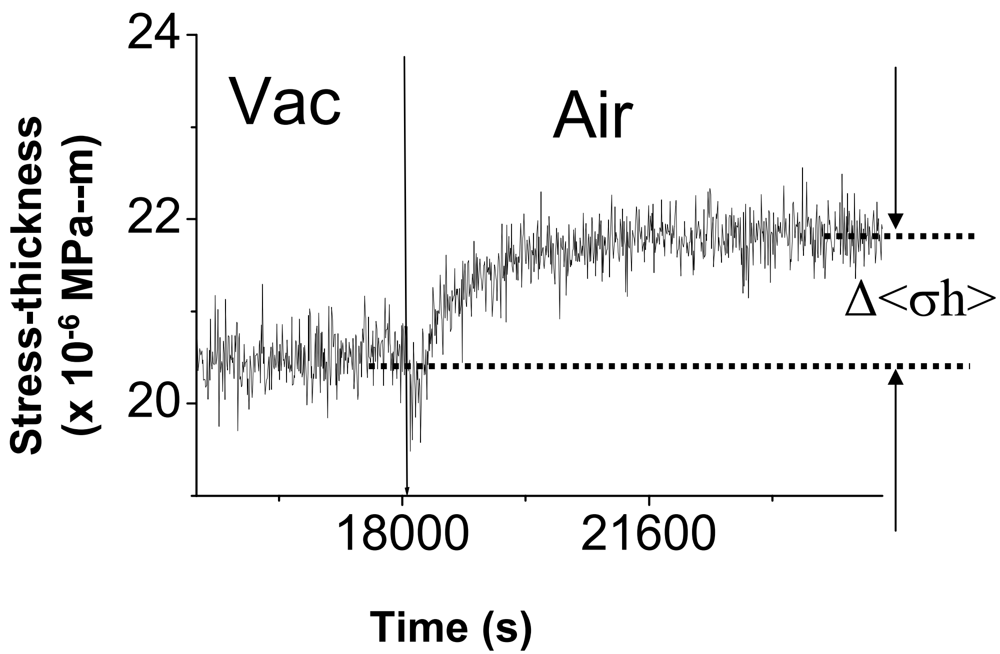
Stress in oxide: measure curvature as oxide grows back



TEM of oxide layer



Change in curvature due to oxide growth



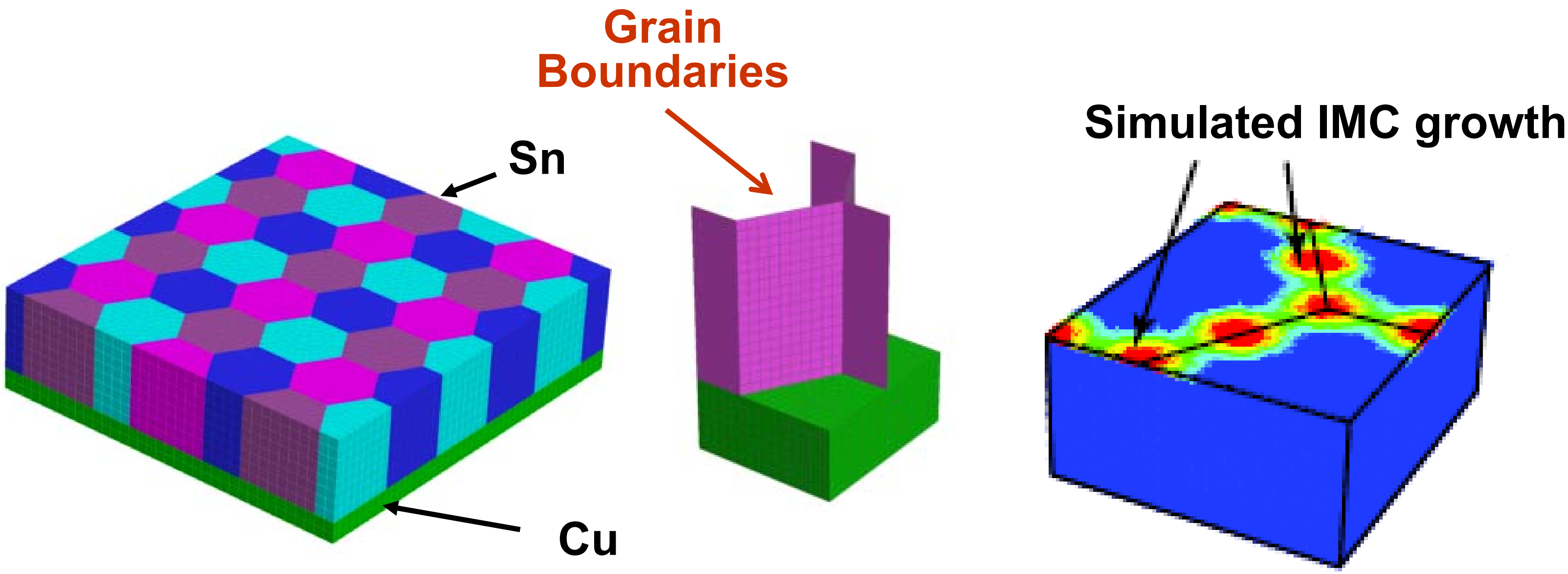
Stress in oxide: *tensile*

$\Delta\langle\sigma h\rangle \sim 1.5 \times 10^{-6}$ MPa-m

$h \sim 5 - 8 \times 10^{-9}$ m

$\langle\sigma\rangle \sim 200 - 300$ MPa

Put it all together in simple model: Model stress evolution/distribution with Finite Element Analysis



Features of model:

- Polycrystalline Sn film
- Columnar microstructure
- Surface oxide
- Cu substrate
- IMC at Sn/Cu interface in triple junction

Options for mechanical behavior:

- Isotropic Elasticity
- Isotropic Plasticity
- Stress-driven, grain boundary diffusion

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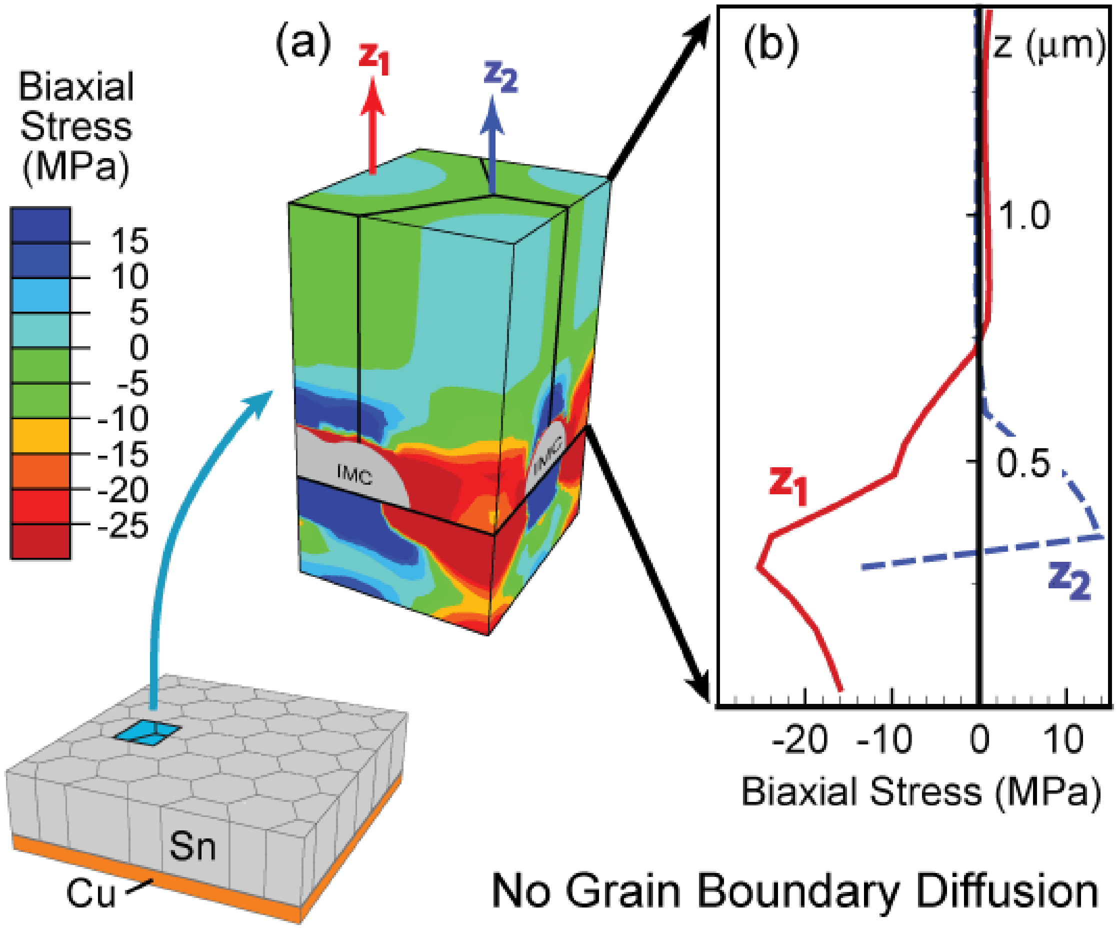
Calculate stress in Sn as IMC "grows"

*e.g. elastic/plastic with **no** g.b. diffusion*



No Grain Boundary Diffusion

With no grain boundary diffusion:

- Compressive stress near IMC

- Plastic zone localized near IMC/Sn interface

-Small stress at surface

(Even more localized if purely elastic, i.e., no plasticity)

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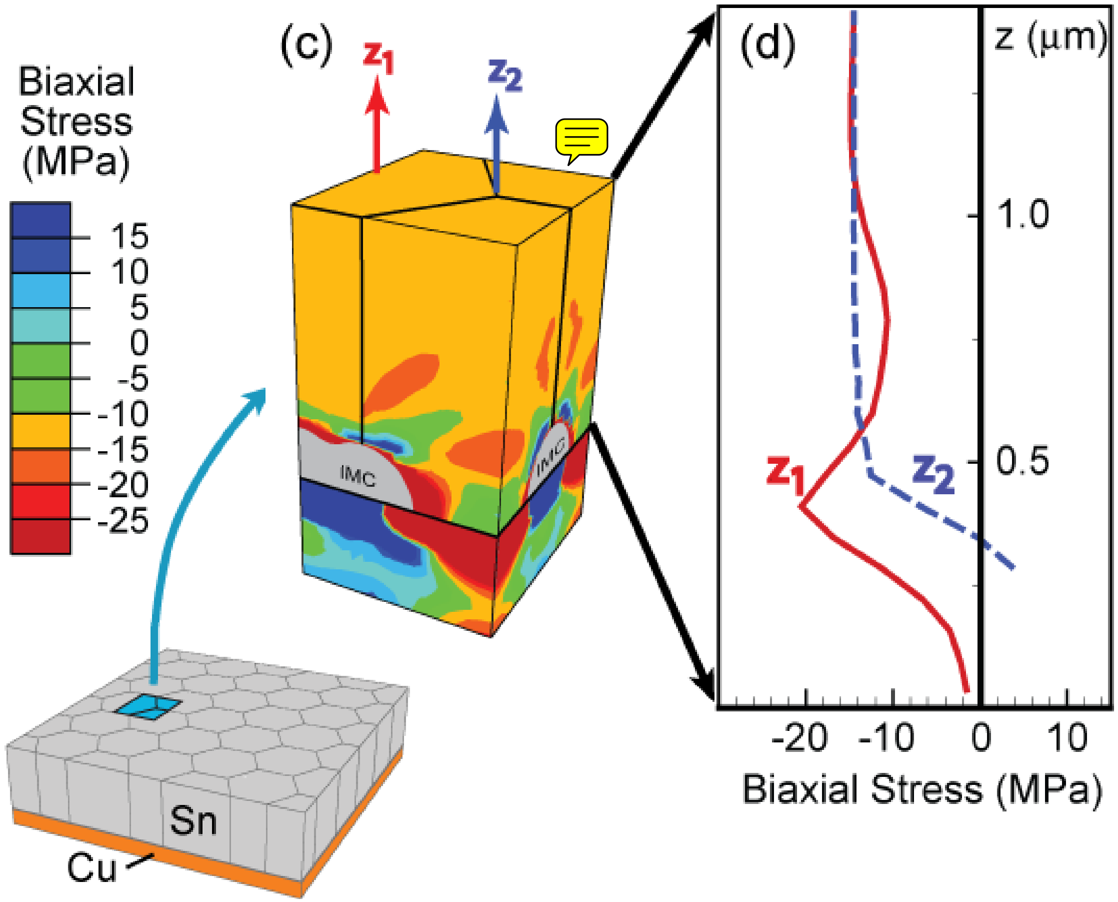
Calculate stress in Sn as IMC "grows"

*e.g. elastic/plastic **with** g.b. diffusion*



With grain boundary diffusion:

-Compressive zone spreads out from IMC

- Uniform plastic zone throughout Sn layer

- Larger stress at surface with g.b. diffusion

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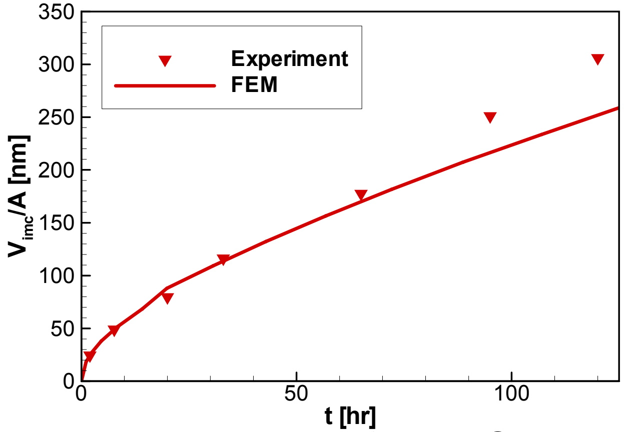
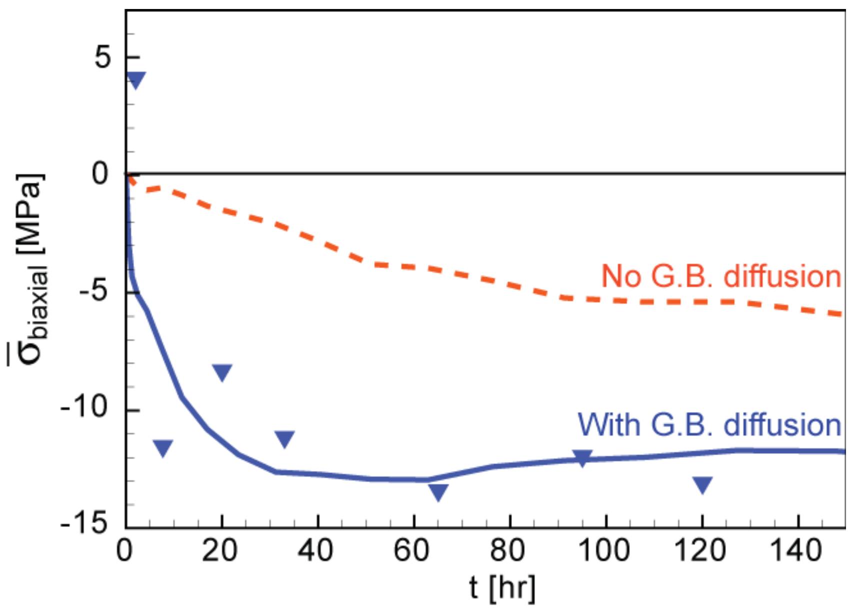
Evolution of average stress with different relaxation mechanisms

IMC growth kinetics



Average stress in Sn from FEA



- Use IMC growth kinetics from experiments

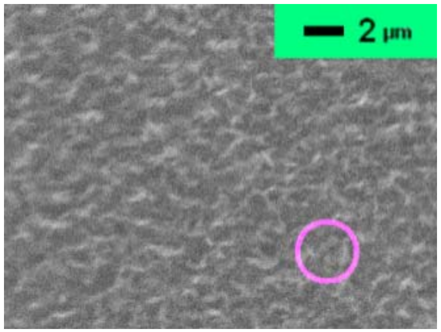
- Calculate average stress over Sn thickness (like measurement)
  - *no g.b. diffusion*
  - *with g.b. diffusion*

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

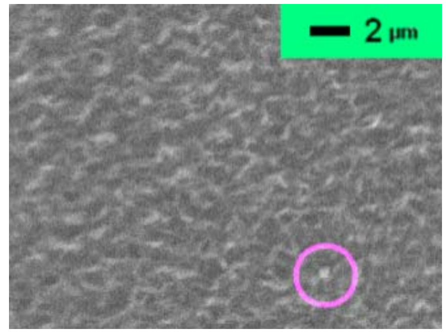
→ FEA & measurements suggest stress spreads across layer as IMC grows due to plasticity and g.b. diffusion

How do whiskers grow?

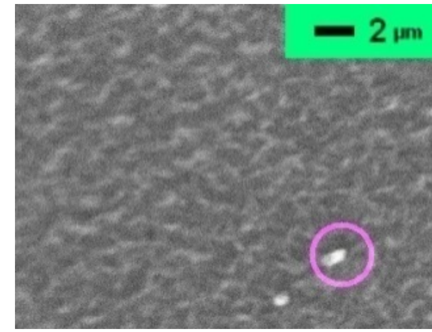
Look at SEM movies of real-time whisker formation over 5 days
Circle placed around whisker root



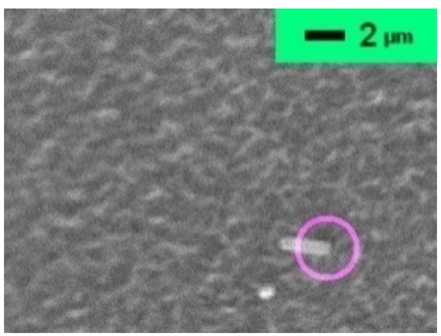
11 hrs



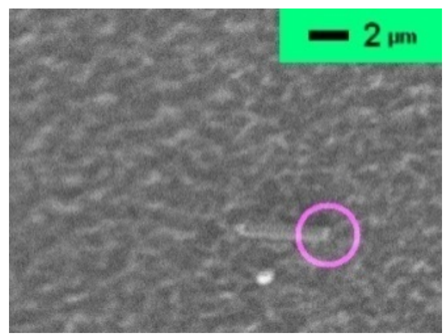
13 hrs



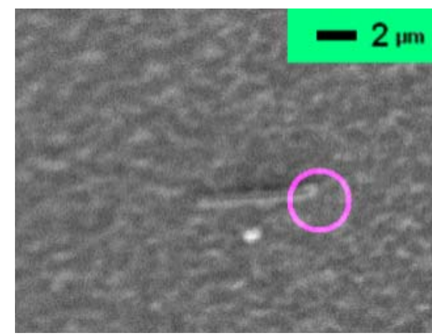
24 hrs



26 hrs



29 hrs



34 hrs

-Growth non-uniform with time
-Outstanding question: Why do they form where they do?
No obvious surface feature before whisker forms

Stress builds up → Why does whisker pop out?

Possible mechanism: Whisker nucleates at "weak" grain

"Weak" means the grain can support a lower maximum stress than its neighbors

Possible reasons for "weak" grains:

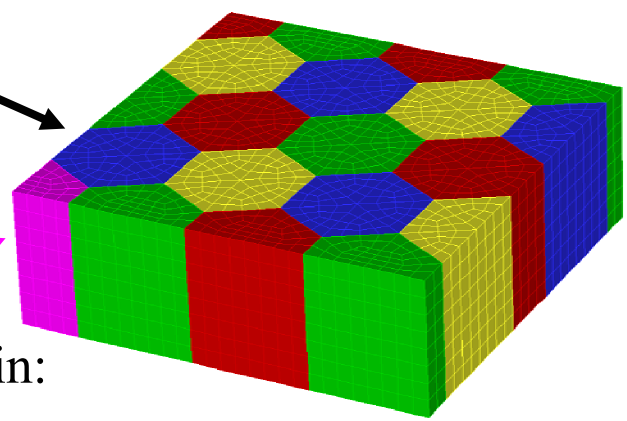
- lower yield stress (e.g., grain misorientation)
- non-columnar grain structure
- presence of horizontal boundaries

(also proposed by others, e.g., Boettinger, Smetana)

- weak oxide

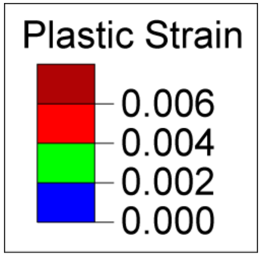
Extend FEA to model whisker growth kinetics

Normal grains: yield strength σ_y



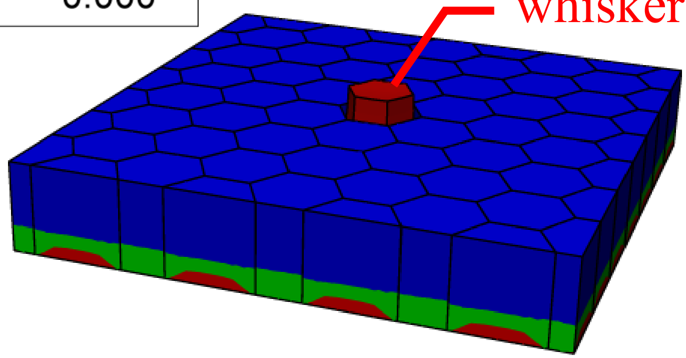
"weak" whisker grain: yield strength $\sigma_w < \sigma_y$

- Periodic array of "weak" whisker grains ($\sigma_w = 0.2\ \sigma_y$)
- Apply uniform expansion of IMC at constant rate
- Allow stress relaxation via elastic/plastic, g.b. diffusion, whisker extrusion



FEA results for different rates of IMC growth

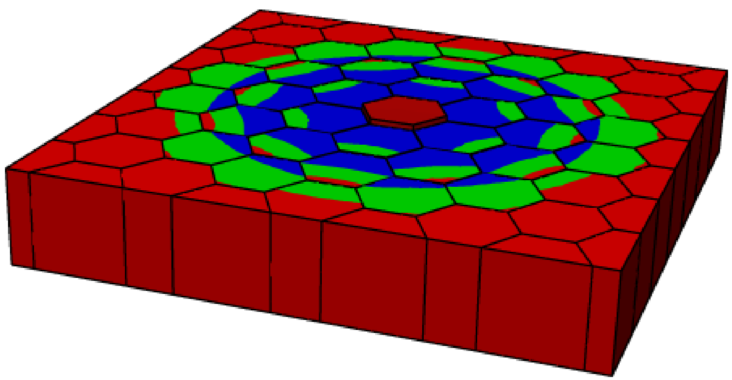
Ratio of IMC growth to diffusion is key factor



Total V_{imc} is identical

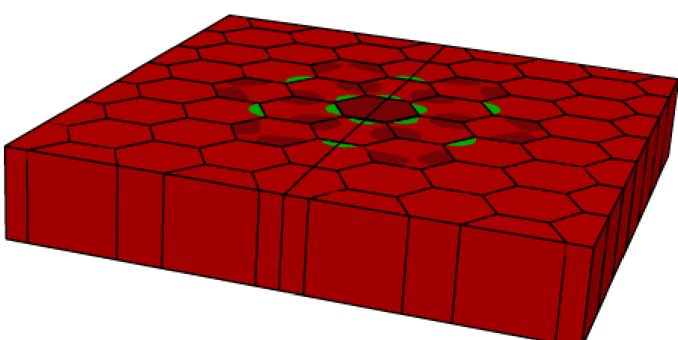
Slow IMC growth rate

- Whiskers remove volume
- Little strain in layer except at whisker



Intermediate IMC growth rate

- Relaxation in region around whiskers
- Remainder of film deforms plastically
- Radius depends on IMC growth

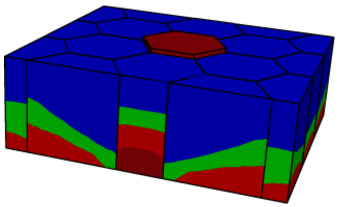


Fast IMC growth rate

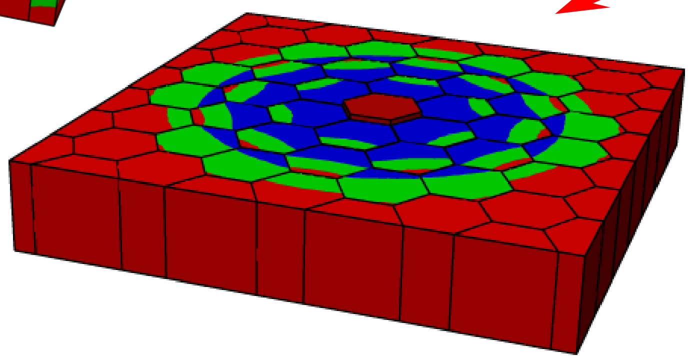
- Film deforms plastically
- Whisker has little effect
- IMC grows so fast, atoms can't diffuse to whisker to relieve stress

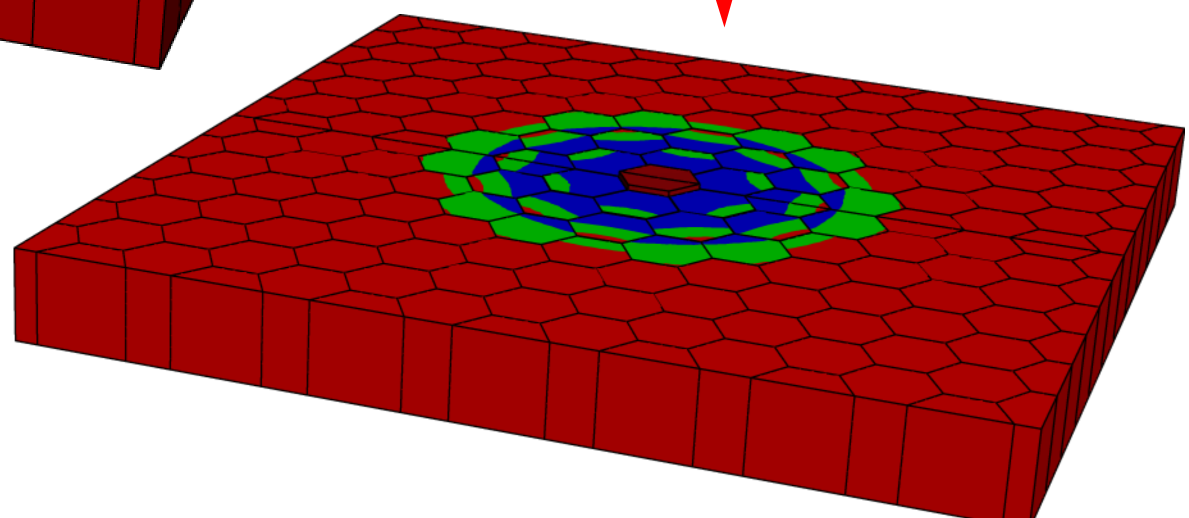
Effect of Whisker Density

Neighboring diffusion fields overlap



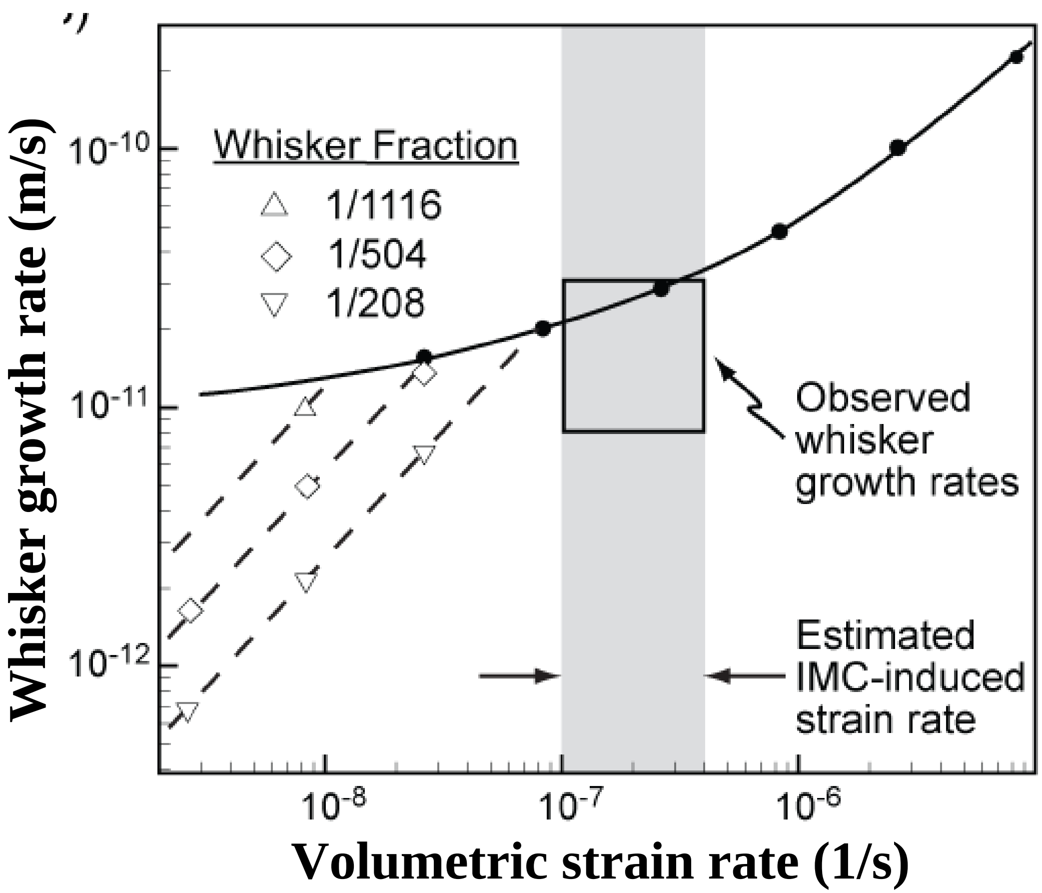
- No neighbor interactions
- Same diffusion radius





IMC growth rate and total (V_{imc}/A) same in all cases.

Whisker growth rate from FEA model



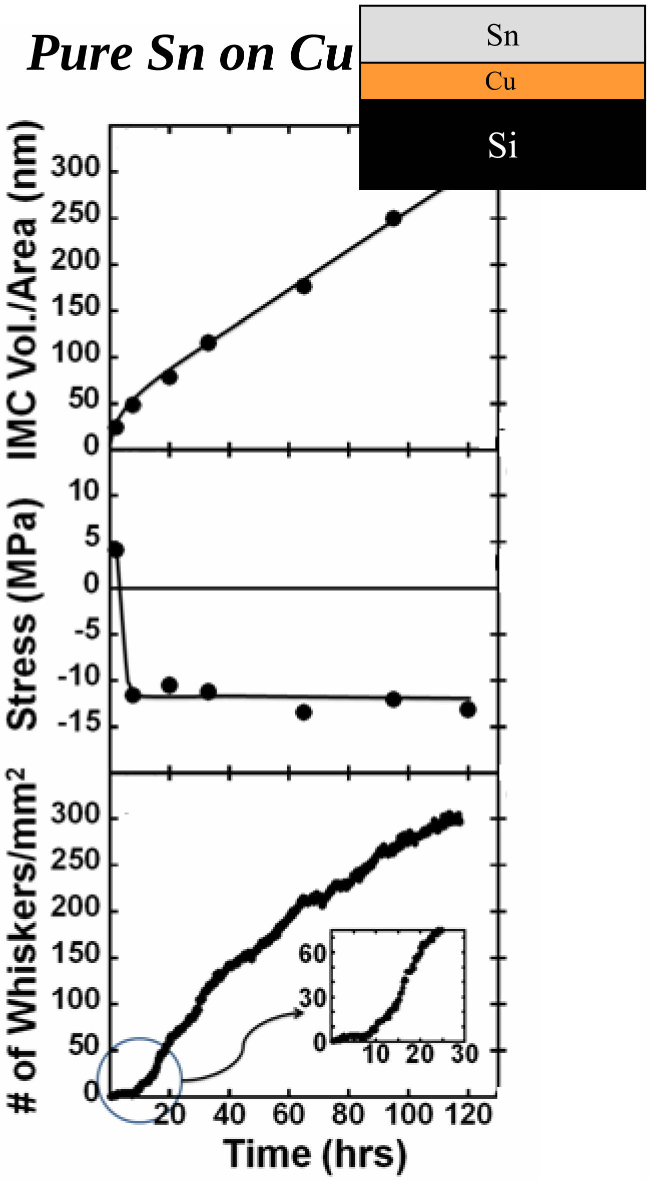
Whisker growth rate depends on:
- strain rate (IMC growth)
- whisker density
- relaxation processes
  - *g.b. diffusion*
  - *yield stress*

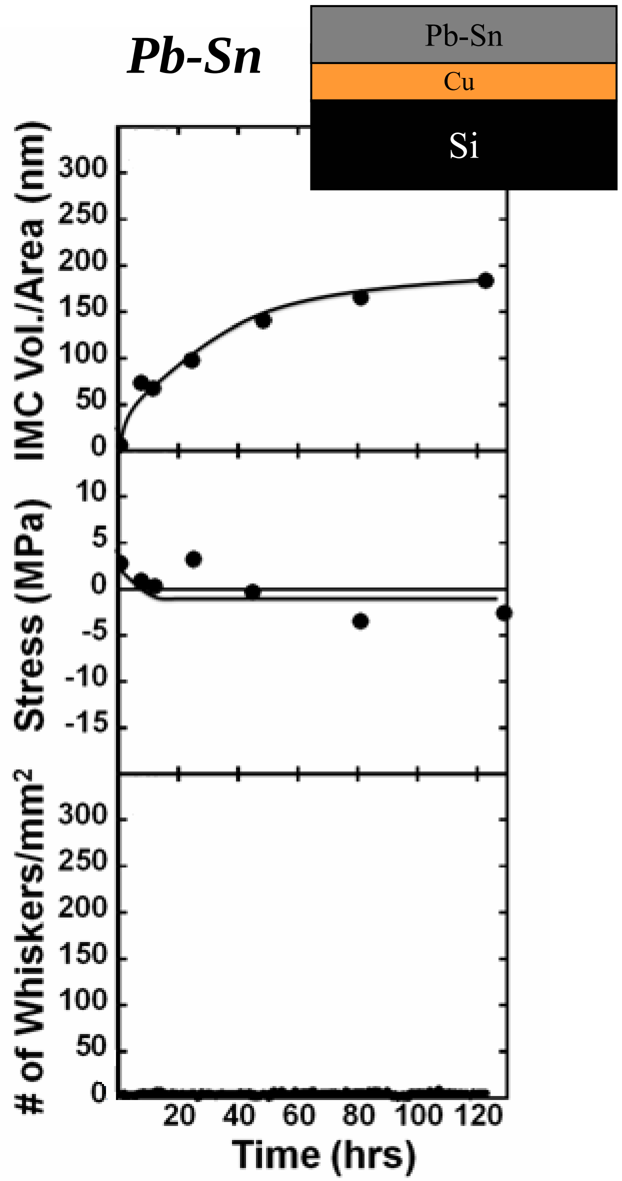
Fast IMC growth/low density
- whisker growth rate depends weakly on IMC
- stress relaxation determined by other processes

Slow IMC growth/high density
- whisker growth relaxes volumetric strain

Observed whisker and IMC growth rates in experiments suggest whiskers do not determine stress in Sn

How does Pb modify IMC/stress/whisker evolution?





Pb-Sn

-IMC growth rate similar to pure Sn

Pb doesn't change IMC growth

-Stress much lower than pure Sn

Pb enhances stress relaxation

-Whisker density lower

-Reduce stress/ fewer whiskers

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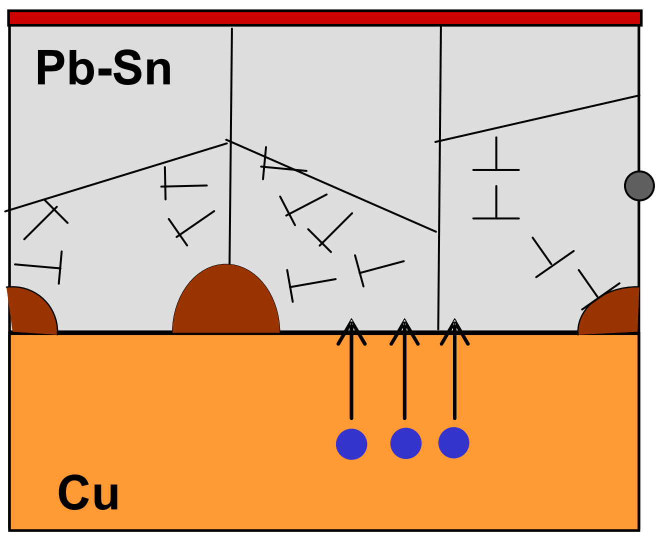
Possible reasons for enhanced relaxation difference

Change in Sn layer microstructure

Pb-Sn

Cu

Addition of Pb to Sn creates more equiaxed structure (e.g. Boettinger et al)



Horizontal grain boundaries are sinks for dislocations, displaced atoms

- accommodate strain but relieve stress

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Implications of our work for whisker mitigation

- Enhance stress relaxation in Sn

- ***don't strengthen Sn!***

- Modify microstructure of Sn or IMC

- ***promote horizontal GB's as sinks for dislocations (enhance relaxation in bulk of film)***
- ***modify IMC growth morphology (create less stress per volume of IMC)***

- Modify oxide

- ***prevent pileup of dislocations***
- ***enhance stress relaxation at top surface***

- Slow down IMC growth

- ***hard to get low enough***
- ***diffusion barriers: kinetically suppresses IMC but don't stop driving force for whisker formation (susceptible to cracking, thermal cycling)***

Summary

1) Kinetic evolution of IMC growth/stress/whisker density

- *Compressive stress builds up in Sn layers*
- *Onset of whisker formation after stress saturates*
- *Stress saturates even though IMC continues to grow (importance of plastic deformation)*

2) Measurements of stress relaxation/generation mechanisms

- *Emission of dislocations around IMC particles (subgrain boundary formation)*
- *Diffusion enables long-range transmission of strain*
- *Oxide critical in buildup of stress*
- *Power law creep in Sn (see addendum)*

3) FEA models of stress/whisker formation

- *Balance between relaxation processes and whisker growth*
- *Suggest relaxation occurs via elastic/plastic/g.b. diffusion at typical whisker densities & IMC growth rates*

Bibliography

Recent whisker-related research from Brown University:

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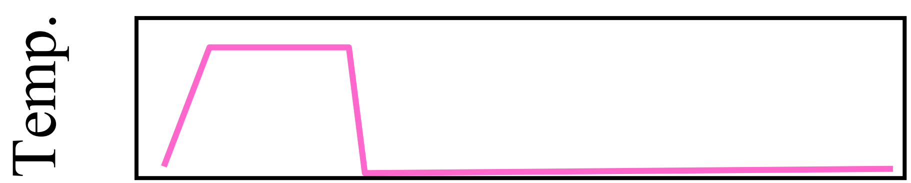
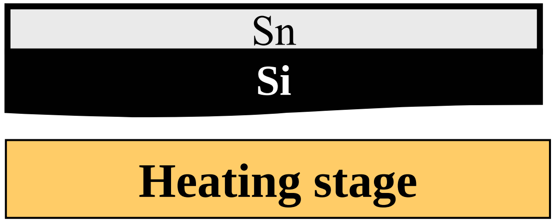
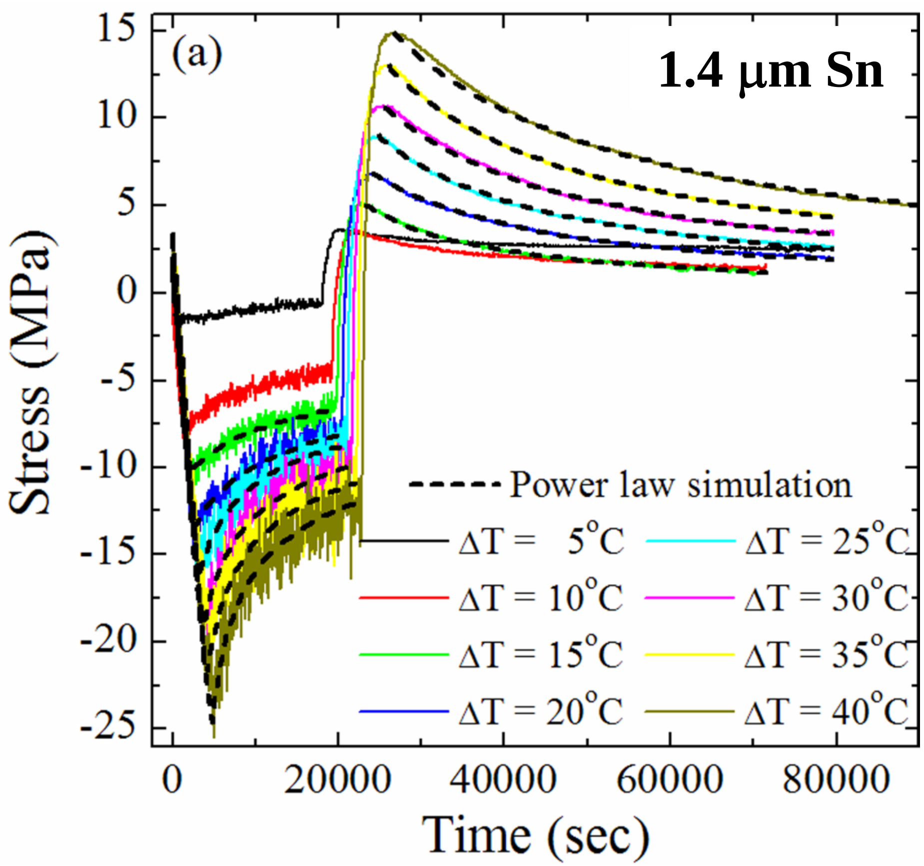
2. **E. Chason, N. Jadhav, W.L. Chan, L. Reinbold and K. S. Kumar, "Whisker formation in Sn and Pb-Sn coatings: role of intermetallic growth, stress evolution and plastic deformation processes", *Appl. Phys. Lett. 92*, 171901 (2008).**
3. **K. S. Kumar, L.Reinbold, A. F. Bower, E. Chason "Plastic deformation processes in Cu/Sn bimetallic films", *J. Mater. Res*., 2916-2934 (2008).**
4. **J. W. Shin, E. Chason, "Stress behavior of electroplated Sn films during thermal cycling", *J. Mater. Res 24.,1522* (2009).**
5. **E. J. Buchovecky, N. Du, A. F. Bower, "A model of Sn whisker growth by coupled plastic flow and grain boundary diffusion", *Appl. Phys. Lett. 94*, 191904 (2009).**
6. **E. Buchovecky, N. Jadhav, A. F. Bower, E. Chason, "Finite element modeling of stress evolution in Sn films due to growth of Cu_6Sn_5 intermetallic", *J. Elec. Mater.*, in press.**
7. **L. Reinbold, N. Jadhav, E. Chason, K. S. Kumar, "Relation of Sn whisker formation to intermetallic growth: Results from a novel Sn-Cu "bimetal ledge specimen"", *J. Mater. Res*., submitted for publication.**
8. **J. W. Shin, E. Chason, "Compressive stress generation in Sn thin films and the role of grain boundary diffusion", *Phys. Rev*., submitted for publication.**
9. **N. Jadhav, E. Buchovecky, L. Reinbold, K.S. Kumar, A. Bower and E. Chason, "Understanding the correlation between intermetallic growth, stress evolution and Sn whisker nucleation", *IEEE Trans on Pack. Manuf*., submitted for publication.**

Addendum: Measure stress relaxation kinetics directly in Sn

Shin, JMR 2009







Use pure Sn layer on Si substrate

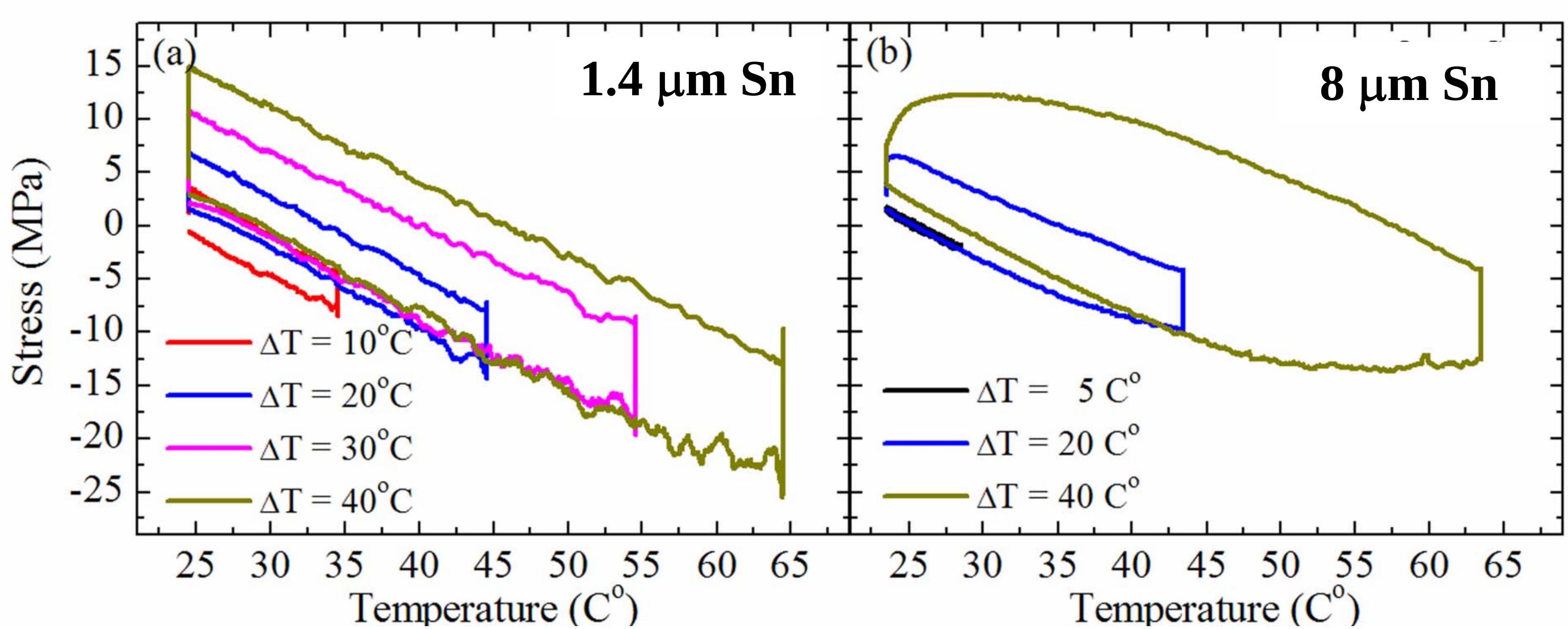
Induce stress with thermal expansion
Measure relaxation for different thickness, composition (Sn, PbSn), temperature range (*ΔT = 5 – 40 °C)*

Results

- Relaxation is power law creep
- More relaxation at higher T
- More relaxation for thicker films (also larger grains)
- More relaxation for Pb-Sn layers

Stress (σ_{avg}) vs. temperature

Linear regime → elastic behavior
Deviation from linear → onset of deformation
Vertical lines show stress relaxation during temperature holding periods



Elastic deformation at lower stresses
Elastic regime extended for thinner films:
- **Thin (1.4 μm) Sn film reaches higher stress than 8 μm Sn**
- **Thick (8 μm) Sn film shows significant relaxation during heating**

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