iNEMI Tin Whisker Workshop, Reno NV, May 29, 2007

Whisker to Hillock Transition: Stress Relaxation Mechanisms in Sn, Sn-Cu, and Sn-Pb Films

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In collaboration with
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Terry Munson of Foresite
Denny Fritz, Gary Latta, and Andy Ganster of Crane/SAIC

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Funded by Crane / Naval Surface Warfare Center

Stress Relaxation in Sn, Sn-Cu, and Sn-Pb Films

- **Sorting through the variables – from the tin whisker literature**
  - **Known necessary conditions for whisker growth**
  - **Unnecessary conditions for whisker growth**
  - **Possible necessary conditions for whisker growth**
  - **Possible effects of Pb on stress relaxation in Sn films**
- **Proposed Experiments at Purdue**
  - **Hillock to whisker transition: composition, stress, microstructure, presence or absence of IMC**
  - **IMC morphologies: why do the tensile stresses develop the way they do given the postulated microstructural changes?**
  - **Changing the stress state at the surface/ disrupting the oxide film**
  - **Separating nucleation from growth**
    - **(Holy Grail of Whisker Studies)**

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Necessary Conditions for Whisker Growth

- Compressive Stress in Film
  - The higher the "better" but how high? Limited by the yield stress in the film. How high should the yield stress be to get whiskers? … to get hillocks?
- Low creep rate in the film
  - But how low, and why?
  - Lower in films than in equivalent "bulk" solder and in Sn-3% Cu alloys, whisker growth is the dominant stress relaxation mechanism – analysis by Boettinger, et al., Acta Materialia, 2005, using model proposed by Tu (1994) and by Hutchinson et al. (2004)
  - Creep is occurring in the elastic regime

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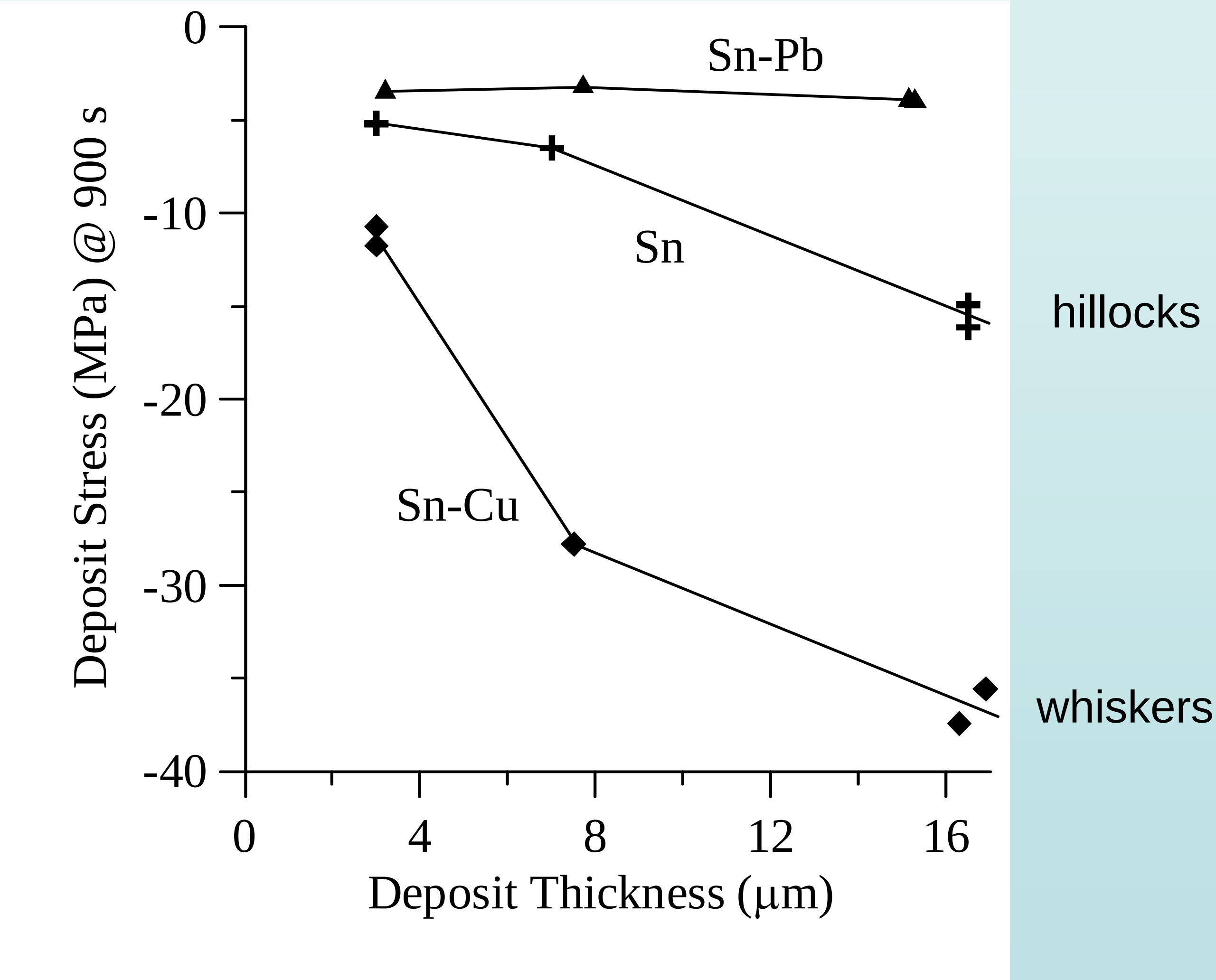
Initial Compressive Stress in Electrodeposits / Whisker Formation

- yield stress
- creep rate
- microstructure evolution
- why should the stresses increase like this? – Chason, Reinhold, Kumar, et al. at Brown
- this is right after plating



Whisker and hillock formation on Sn, Sn–Cu and Sn–Pb electrodeposits, W.J. Boettinger , C.E. Johnson, L.A. Bendersky, K.-W. Moon, M.E. Williams, G.R. Stafford, Acta Materialia 53 (2005) 5033–5050.

Not Necessary Conditions for Whisker and Hillock Growth

- **IMC formation** – Williams, et al. paper on whisker and hillock growth in Sn and Sn-Cu films on tungsten
- **Single-crystal columnar grains** – Moon, et al. paper on effects of Cu on whisker and hillock growth

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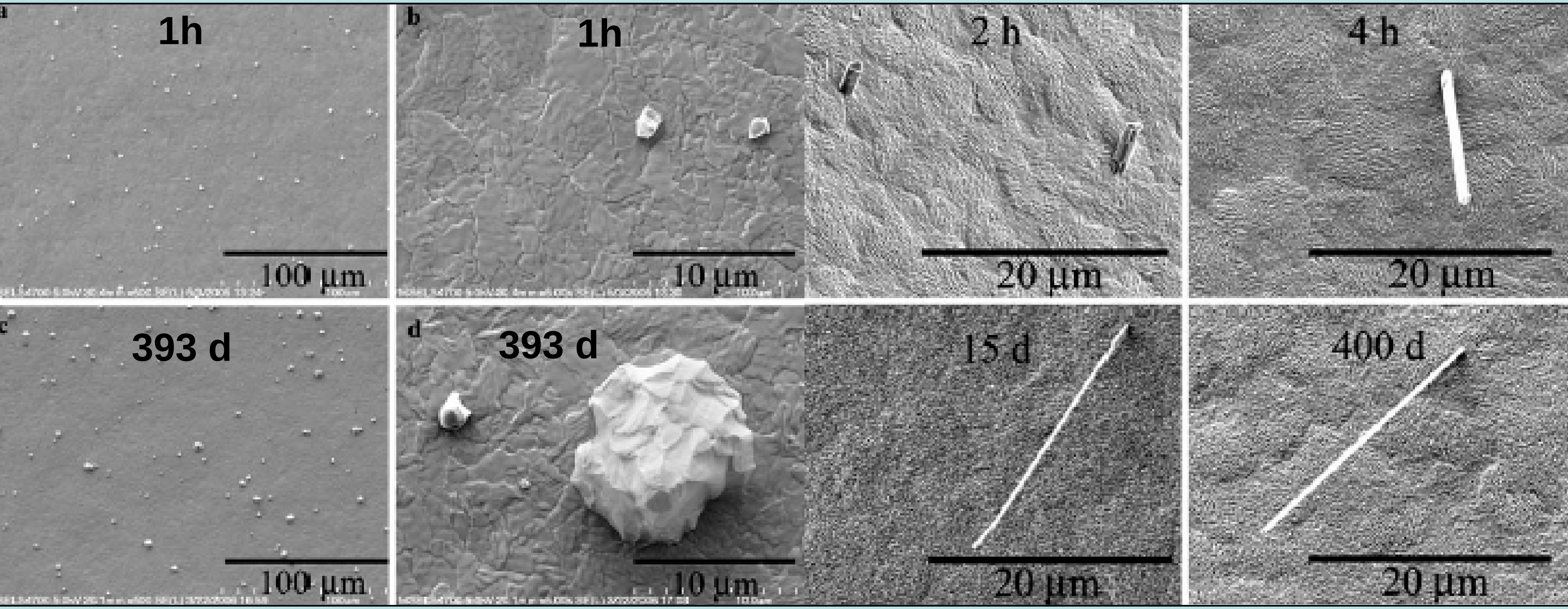

Sn films on tungsten

Sn-Cu films on tungsten

Hillock and Whisker Growth on Sn and SnCu Electrodeposits on a Substrate Not Forming Interfacial Intermetallic Compounds

M.E. WILLIAMS,[1,3] K.-W. MOON,[1] W.J. BOETTINGER,[1] D. JOSELL,[1] and A.D. DEAL[2]

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Journal of Electronic Materials, 2007

Plenty of horizontal and angled grain boundaries; what are the energies of the grain boundaries ?

Preferential precipitation on vertical grain boundaries (gbs) suggests possible differences in interfacial energy between gbs of different orientation and/or in strain energy for oriented precipitation

The Formation of Whiskers on Electroplated Tin Containing Copper

K.-W. Moon, M. E. Williams, C. E. Johnson, G. R. Stafford, C.A. Handwerker, and W. J. Boettinger

Metallurgy Division, MSEL, NIST, Gaithersburg, MD 20899-8555, USA

Proceedings - Pac Rim 2001

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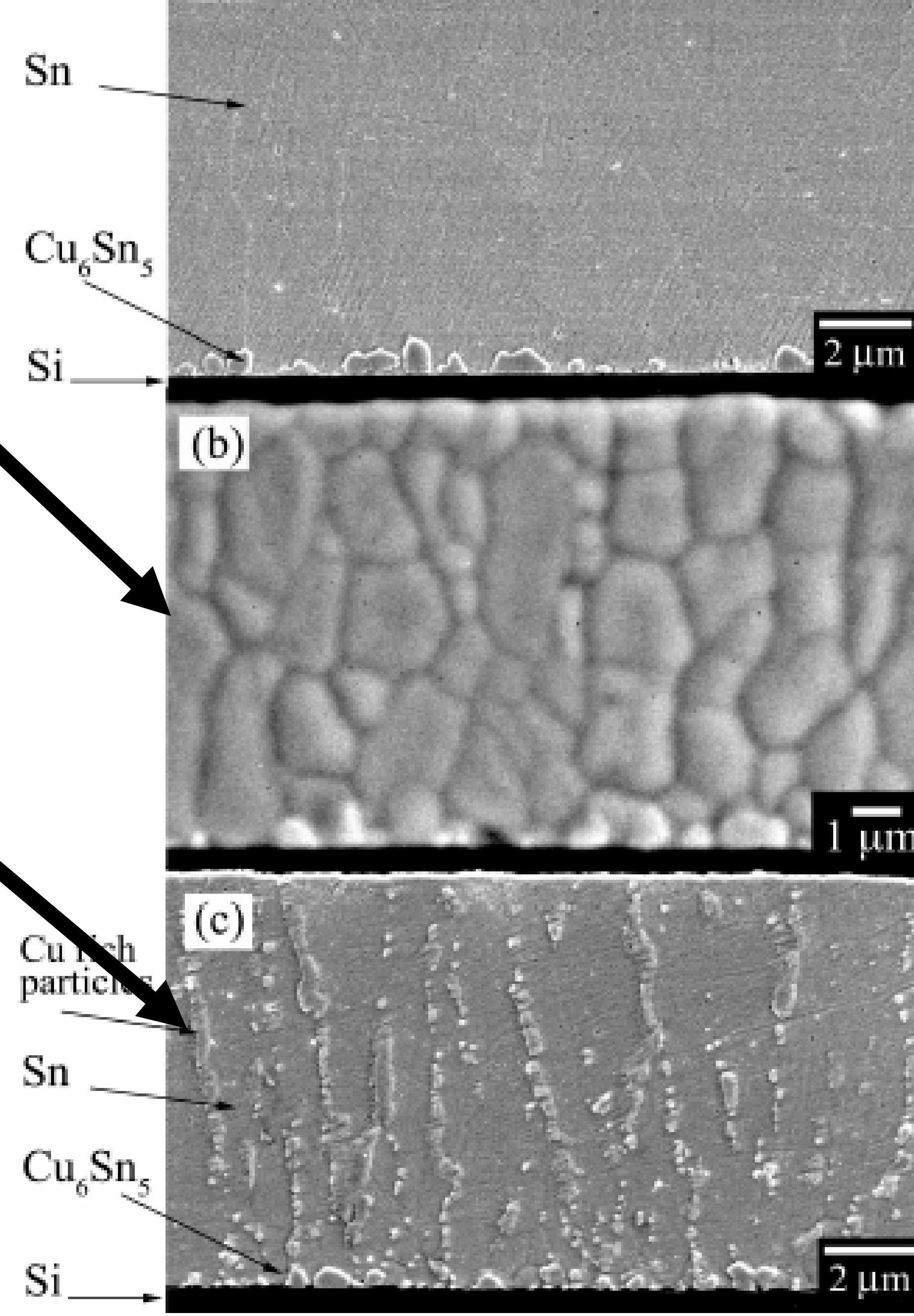

Figure 3. Cross sections of 10 µm thick Sn deposited on Cu evaporat
Si(100): (a) polished pure Sn deposit, (b) pure Sn deposit following 15 s et
in 10 % HCl, and (c) polished Sn-1.5 % mass fraction Cu deposit.

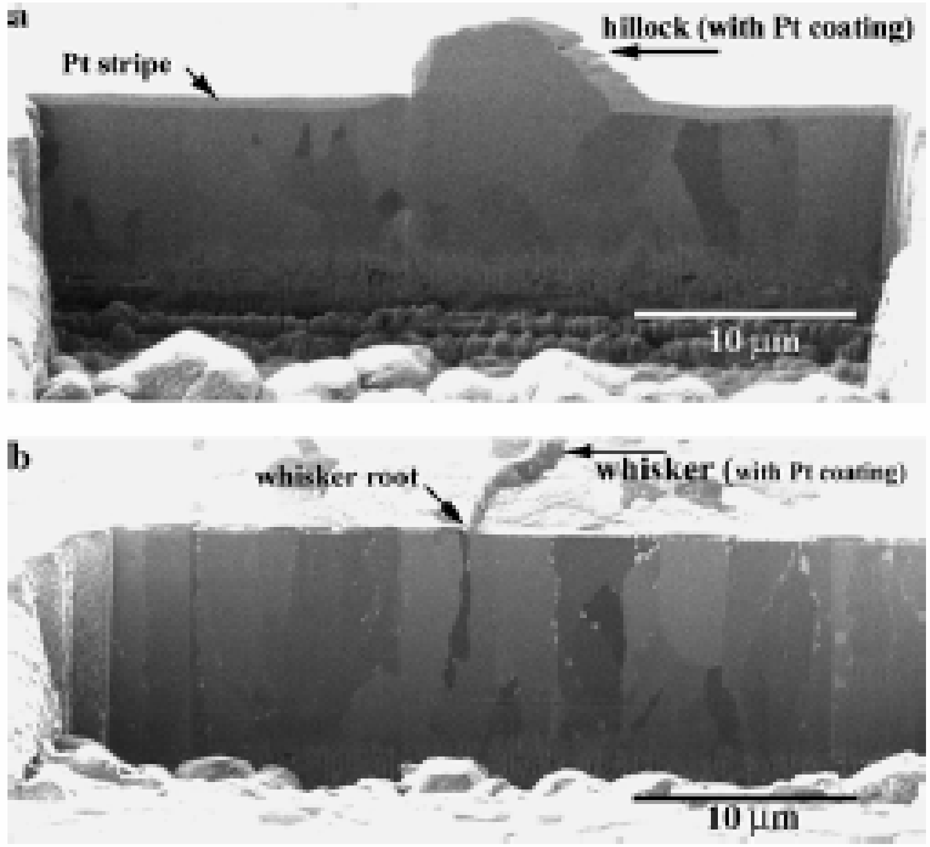

Fig. 5. (a) FIB cross section of a hillock on a 15 μm thick pure Sn electrodeposit on a 0.2 μm Sn seed layer on a W substrate. Note: the hillock and surrounding surface were covered by a 1 μm thick platinum stripe prior to milling. (b) FIB cross section of a whisker on a 15-μm-thick Sn-Cu electrodeposit on a 0.2-μm Sn seed layer on a W substrate. Note: the whisker and surrounding surface were covered by a 1-μm-thick platinum stripe prior to milling.

Hillock and Whisker Growth on Sn and SnCu Electrodeposits on a Substrate Not Forming Interfacial Intermetallic Compounds

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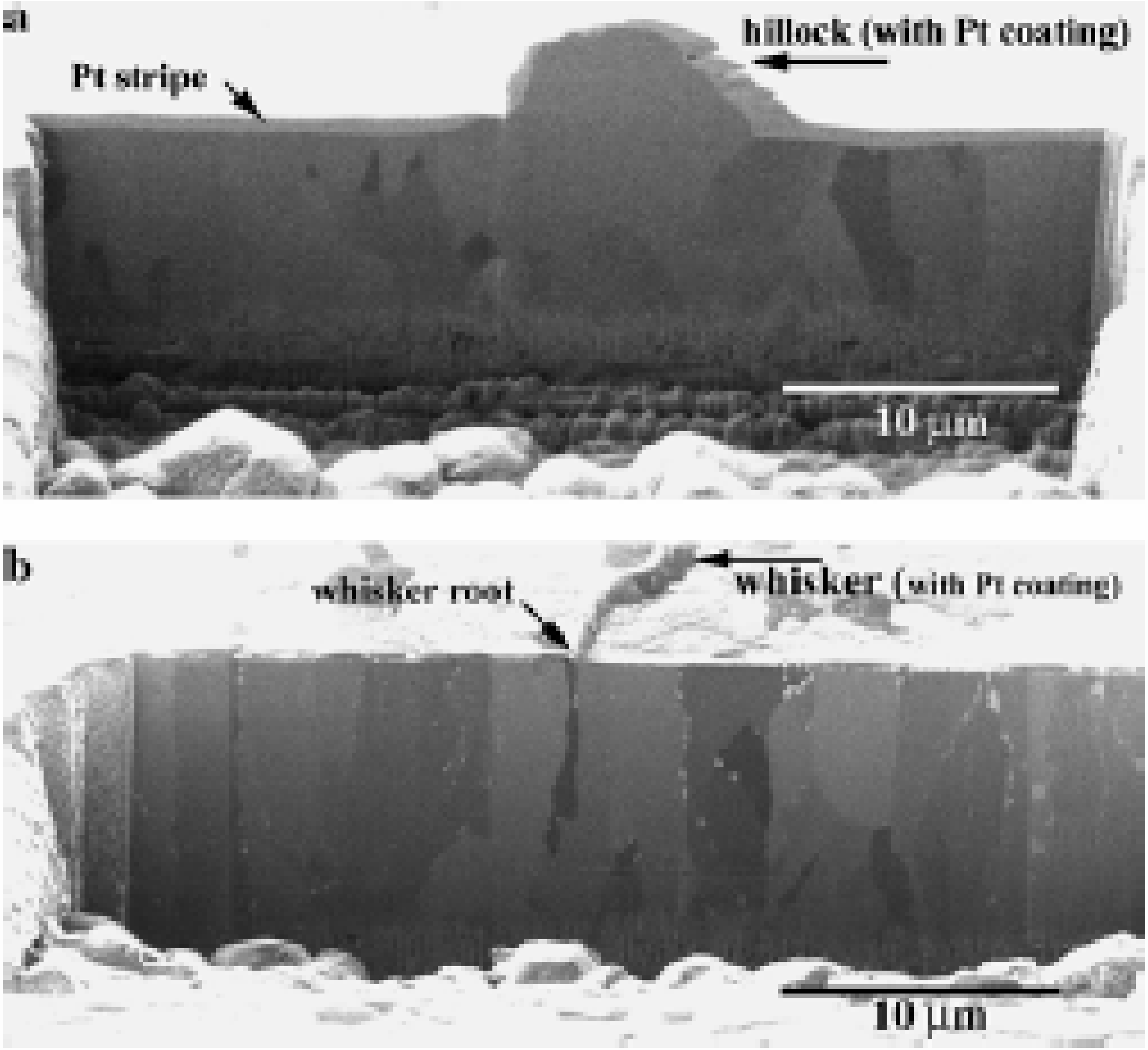
a
hillock (with Pt coating)
Pt stripe
10 µm
b
whisker root
whisker (with Pt coating)
10 µm

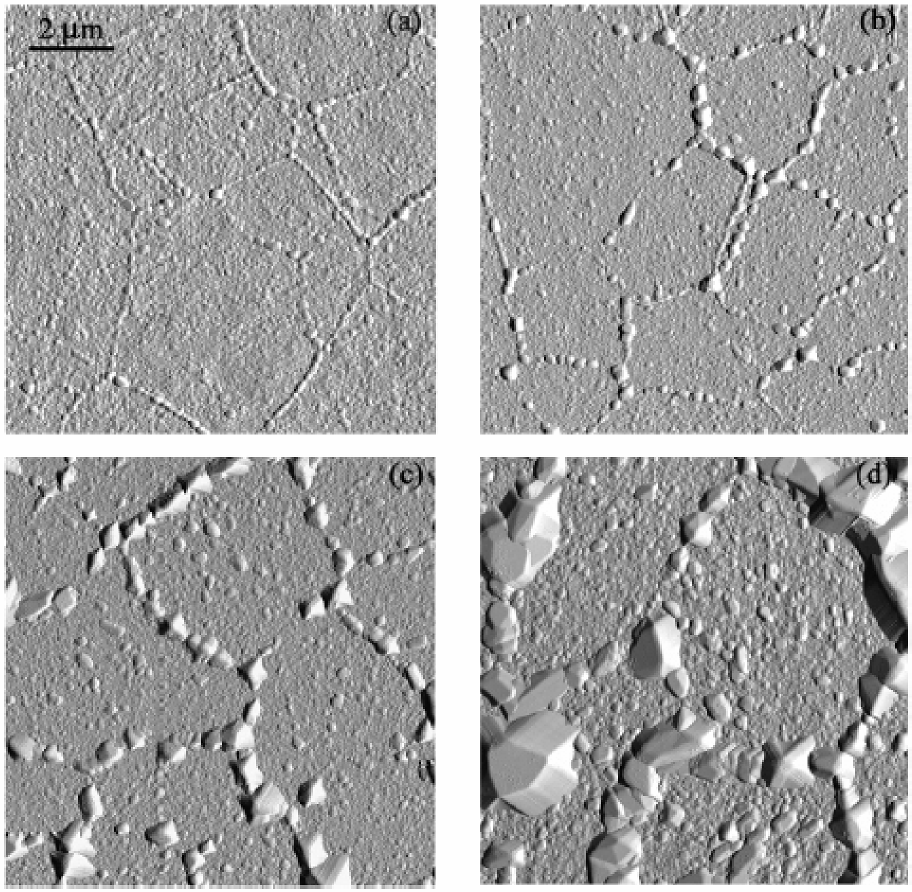

Fig. 4. A typical Sn–Cu IMC growth series on the copper substrate at ambient temperature observed by AFM (10 × 10 μm deflection images). The electroplated matte tin (10 μm) was stripped off after the times of (a) 0.5 h, (b) 2 h, (c) 16 h, and (d) 120 h.

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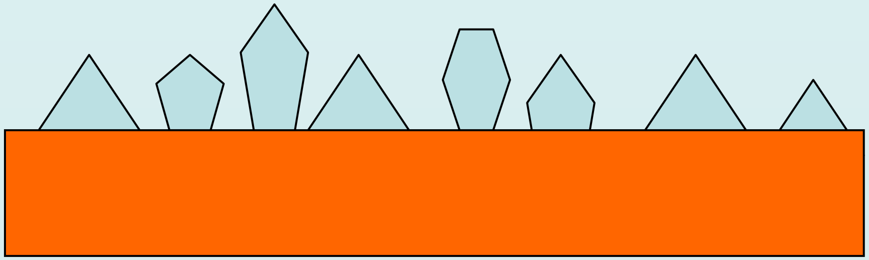
Investigation of Sn–Cu Intermetallic Compounds by AFM: New Aspects of the Role of Intermetallic Compounds in Whisker Formation

Wan Zhang, Andre Egli, Felix Schwager, *Member, IEEE*, and Neil Brown



When the Sn films are stripped off, what makes the resulting stresses in the remaining IMC-Cu tensile?

From Stafford et al., stresses are definitely tensile after tin films stripped off. Also Chason, et al.

From Zhang et al. results, what is the role of the substrate?

Possible effects of Pb on stress relaxation in Sn

Pb changes mechanical behavior

- Higher intrinsic creep rate
- Lower yield stress
- Mitigates impurity effects on mechanical behavior

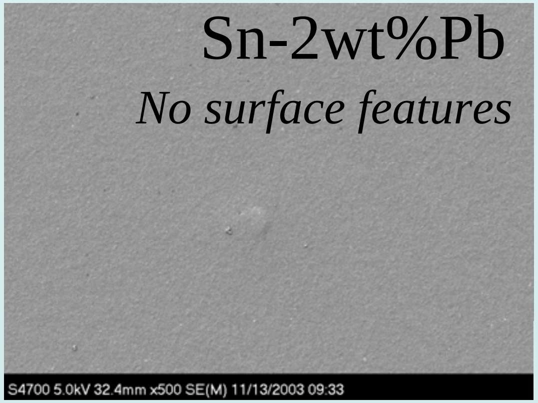
Pb segregates to interfaces

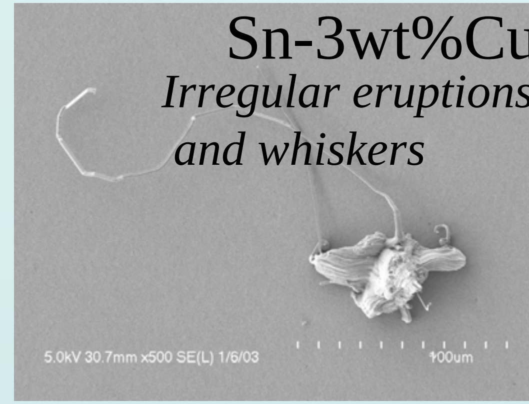
- Increases grain boundary mobility
- Improves efficiency of grain boundary and surface sources and sinks for vacancies in creep
- Weaker or non-continuous surface oxide
- Changes IMC morphology
- Changes interfacial energies and diffusivities

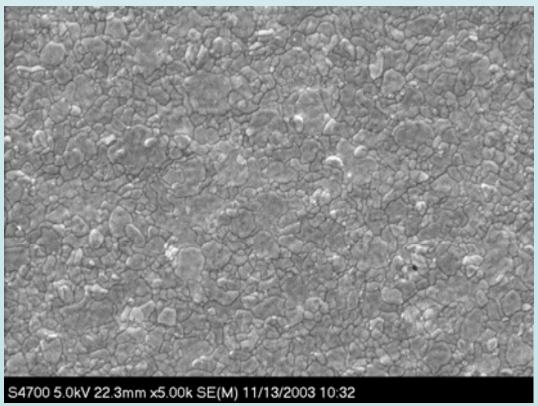
Pb changes electrodeposition behavior

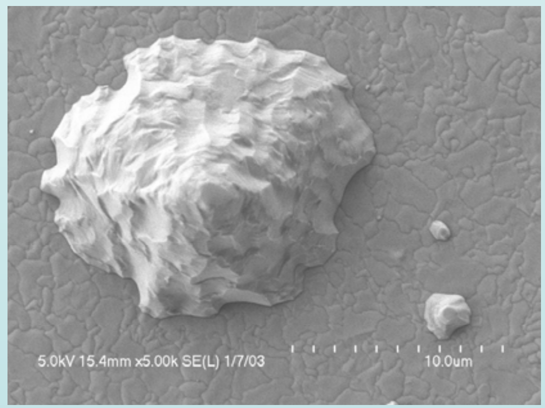
- Increases grain nucleation rate during electrodeposition
- Changes impurity incorporation rate

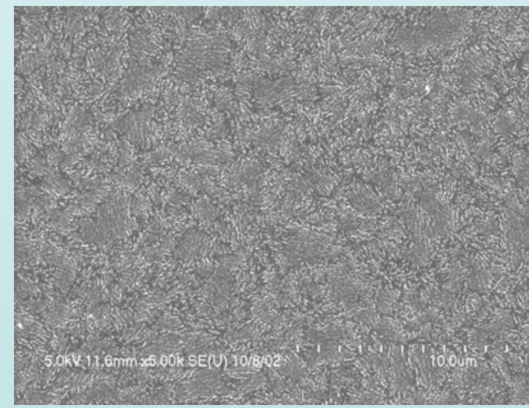
Microstructure of Surface & Interior of 16 μm Thick Deposits @ >100 days

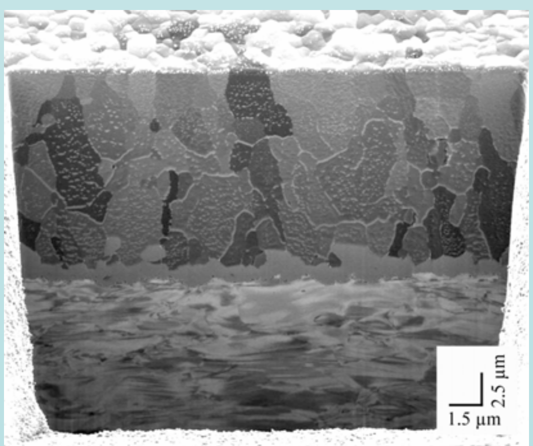


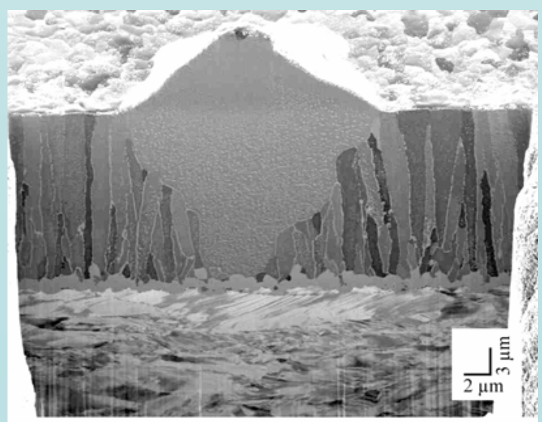


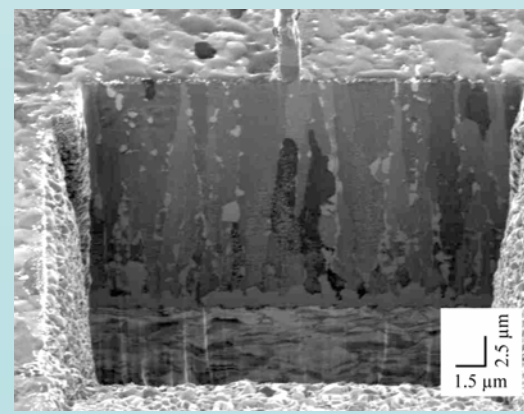












FIB pictures: Galyon and Palmer

Proposed Experiments

- Cantilever experiments as a function of composition for Sn and Sn-Cu – *building on results from the literature*
    - Transition from hillocks to whiskers
    - Well characterized substrates – Cu and W
    - Well characterized IMC-Cu-film interface
    - Characterize grain structure more quantitatively
    - Measure creep behavior by nanoindentation
- Try to disrupt oxide layer, without plastic deformation
    - Use FIB to change local surface condition – effect of Ga a serious issue
    - Change oxide properties using controlled surface impurities/ local corrosion
- **Your input and help requested** – What effects can we isolate? What can we learn about Sn-Pb that might help us learn the limitations of Pb-free systems?

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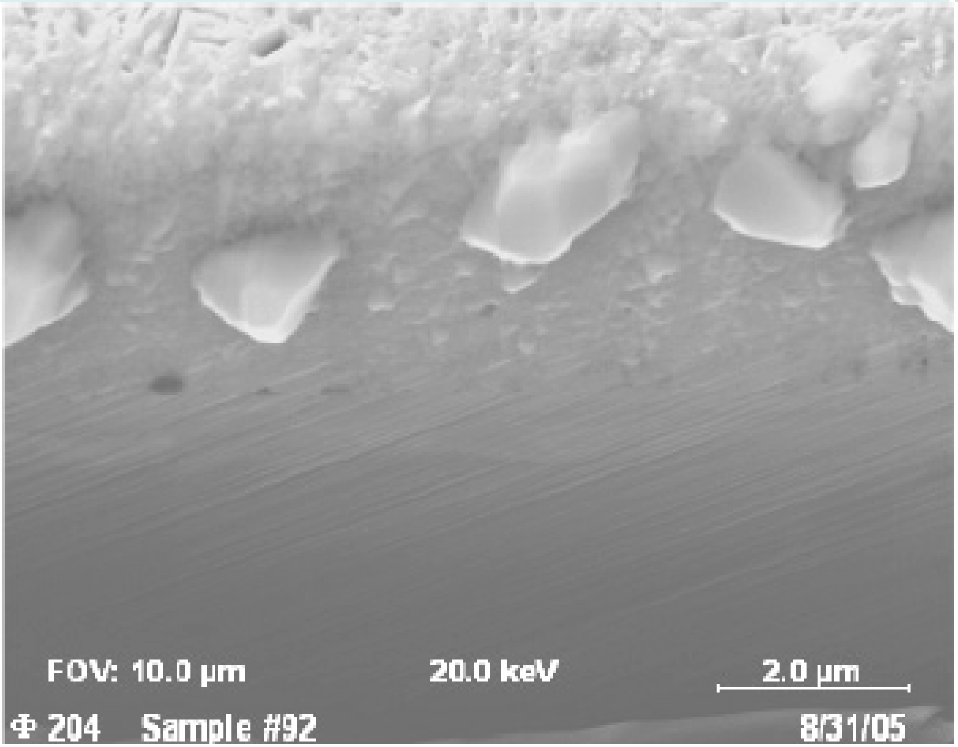

Figure 6. Nodules Forming 30 Minutes after the FIB Microsection was made (FIB Microsection from Figure 4)

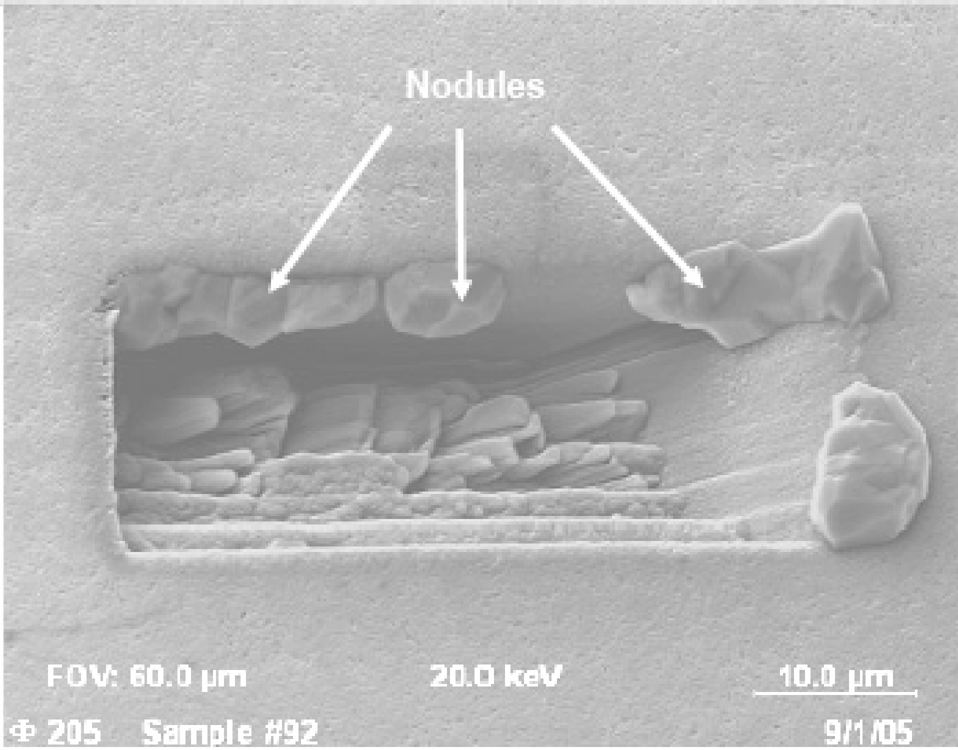

Figure 7. Nodules 18 Hours after the FIB Microsection was made (FIB Microsection from Figure 4)

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TRACER DIFFUSION IN WHISKER-PRONE TIN PLATINGS

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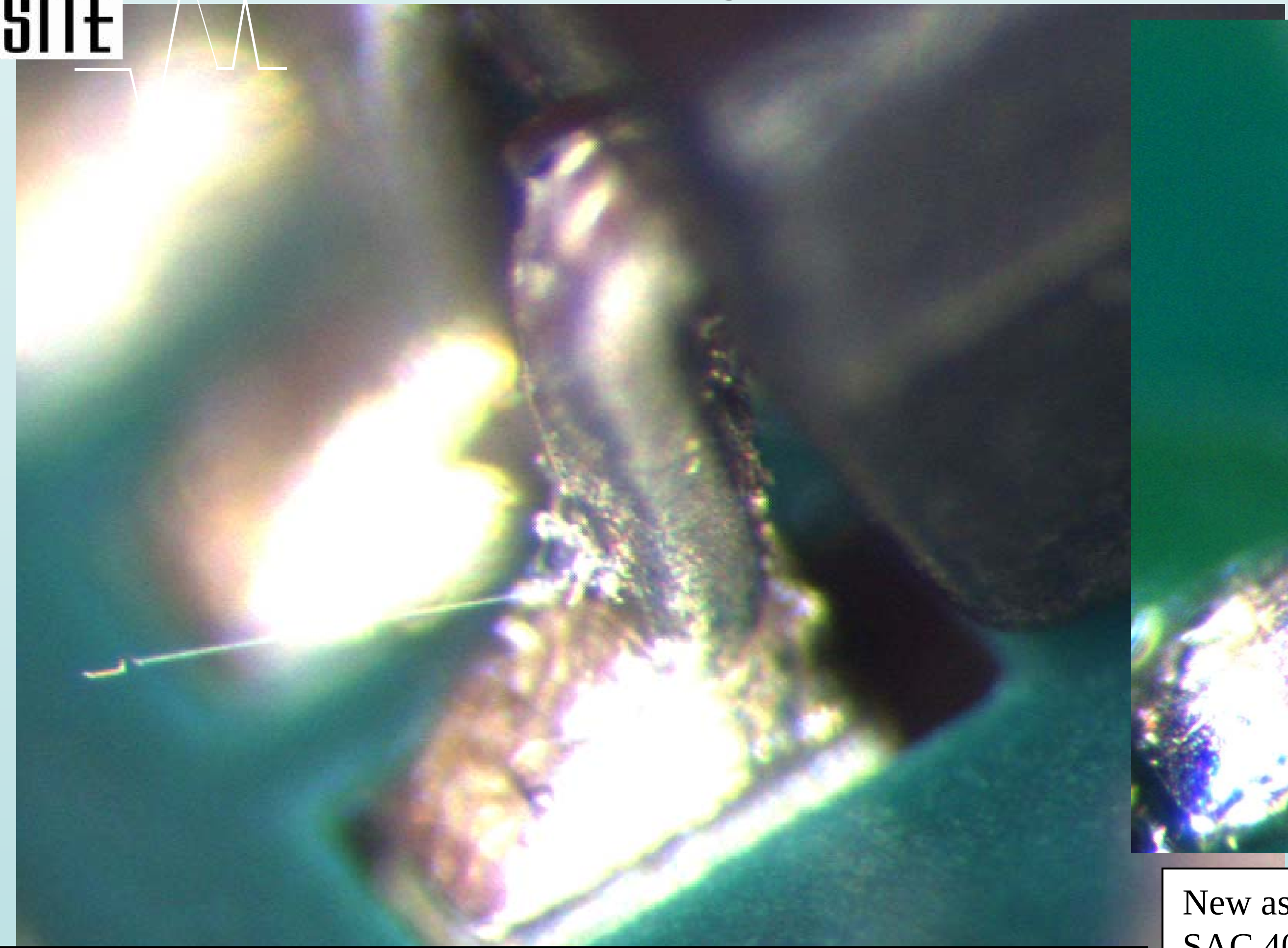
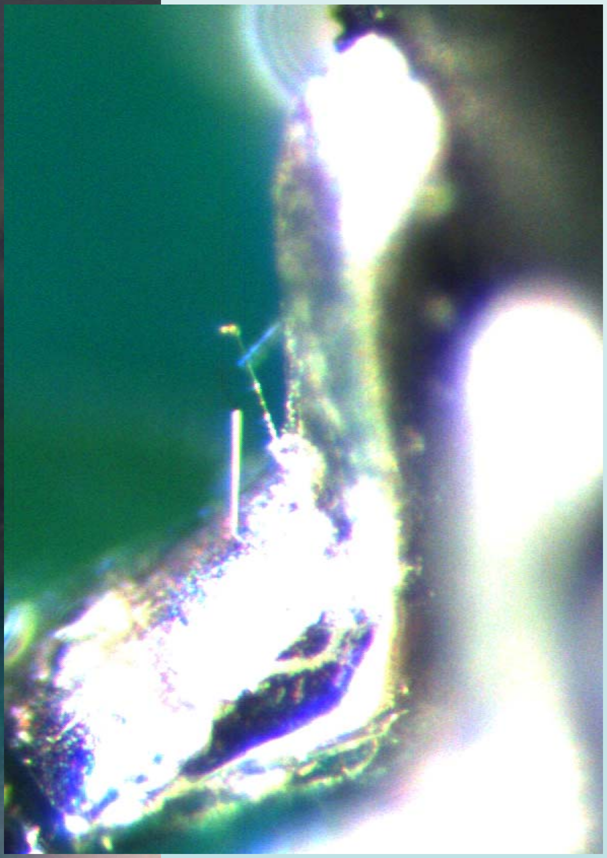
Whiskers Growing from SAC 405 Solder Surface





New assembly using a no clean SAC 405 built week 51 and no life testing exposure and whiskers were found in 4 months from a normal storage environment and only powered to test.

Life tested Assembly with a No Clean solder paste (SAC 405) reflowed (two sided reflow and this was first side) of a MOSFET devices with an Alloy 42 lead frame that was matte tin plated. This assembly was subjected to 20 days of life testing at 65°C and 25% RH with a 40 CFM blower on these assemblies were processed with cyclic load being applied. This unit passed the test but whiskers were observed after the test. This product was built in 2005 week 46.

At first sight, it appears that the boards, which had the flux removed have less whisker growth compared to boards with a nonclean flux. Unfortunately, due to the limited amount of whiskers found on the board-assembled units, it is difficult to state this with certainty. It would concur with the observation made in Japan that abietic acid, which is an ingredient of many flux types, promotes corrosion [15].

Next to the two earlier found mechanisms for whisker growth, related to typical field life conditions of semiconductor devices, i.e., CTE mismatch and irregular growth of intermetallics, a third mechanism for whisker growth is found: oxidation and corrosion of the Sn layer.

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Humidity Effects on Sn Whisker Formation

Pascal Oberndorff, Marc Dittes, Paolo Crema, Peng Su, and Elton Yu

- **Your input and help requested** – What effects can we isolate? What can we learn about Sn-Pb that might help us learn the limitations of Pb-free systems? Did nature give us another “magic” additive like Pb?

- Carol Handwerker: handwerker@purdue.edu 765-494-0147
- Aaron Pedigo: aepedigo@purdue.edu

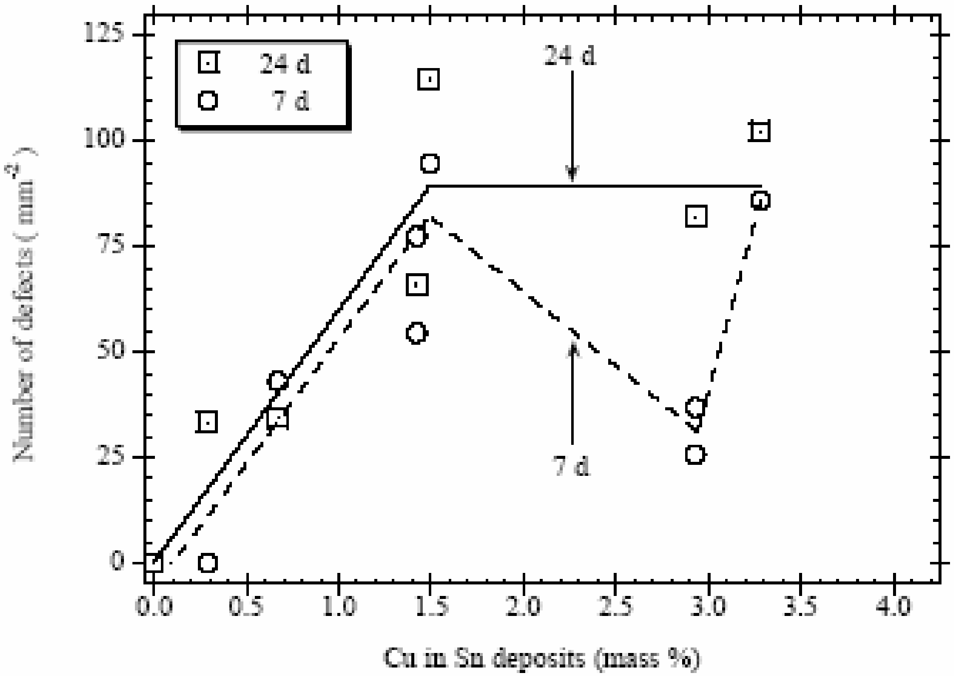

Figure 6. Number of defects (eruptions and whiskers) as a function of Cu content in the Sn-Cu deposit on the pyrophosphate Cu substrate for two aging times. Each data point is the average defect density from several locations on the electrodeposit. (See Table 1 for error ranges.)

Table 1. Summary of all measurements in Figure 2, 5, and 6.

Cu^{2+} in electrolyte (mol/L)	Cu in deposit (mass %)	Sn surface grain size (µm)	Defect number (mm^{-2}) 7 d	Defect number (mm^{-2}) 24 d
0	0	0.64 ± 0.05	0	0
0.00050	0.29 ± 0.33	0.60 ± 0.05	0	33 ± 25
0.00275	0.67 ± 0.38	0.57 ± 0.06	43 ± 22 43 ± 15*	34 ± 26
0.00500	1.49 ± 0.42	0.58 ± 0.10	95 ± 30*	115 ± 52
0.00750	1.42 ± 0.45	0.55 ± 0.09	55 ± 27 78 ± 26*	66 ± 41
0.01500	2.93 ± 1.15	0.31 ± 0.03	37 ± 30 26 ± N/A*	82 ± 47
0.02500	3.28 ± 0.92	0.19 ± 0.02	86 ± 15*	102 ± 58

* Only 3 regions were measured.
N/A: not available.

Number and types of defects – hillocks to whiskers and eruptions – change as a function of copper concentration in the deposited film

The Formation of Whiskers on Electroplated Tin Containing Copper

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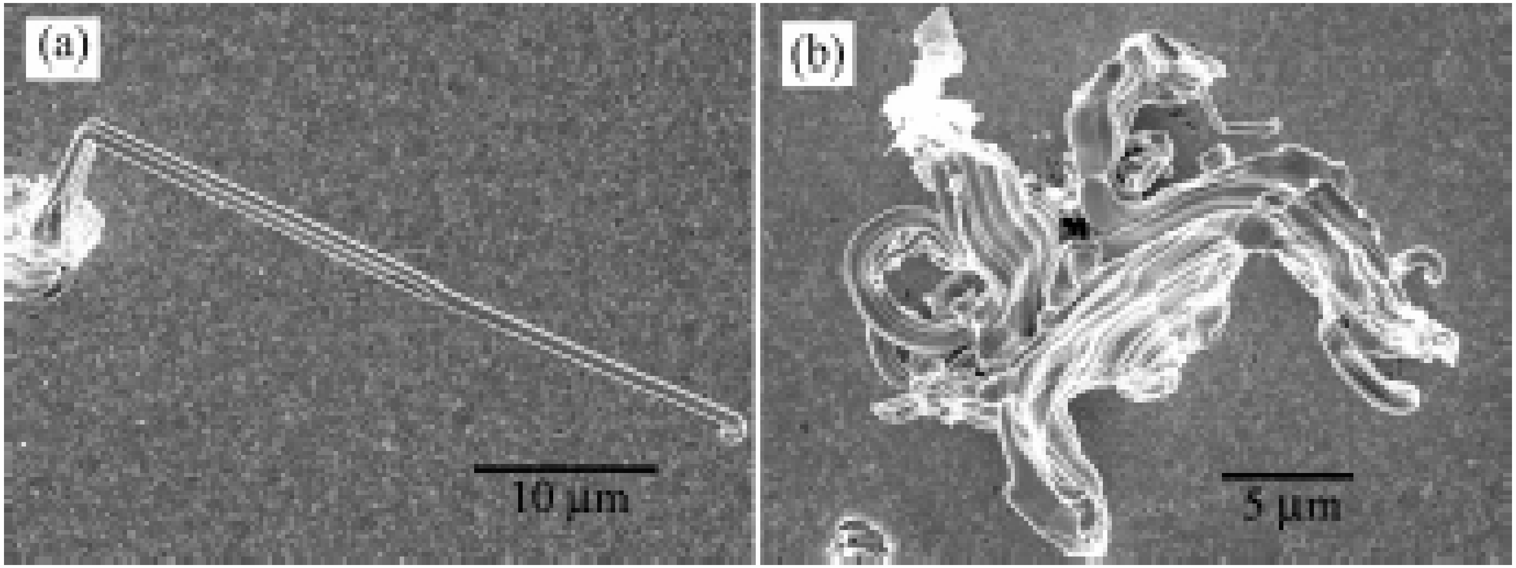

Figure 1. Types of defects on the Sn deposit: (a) a filament type Sn whisker and (b) a Sn eruption with small length whiskers.

Table 2. Lengths of the longest Sn whisker measured as a function of alloy composition and aging time. The substrate was a 250 µm thick copper film electrodeposited from a pyrophosphate electrolyte.

Mass fraction Cu (%) in deposit	Whisker length (µm)	
	7 d	24 d
0	N/W	N/W
0.29	N/W	1
0.67	4	4
1.49	55	44
1.42	59	190
2.93	24	160
3.28	19	181

N/W: no whisker observed

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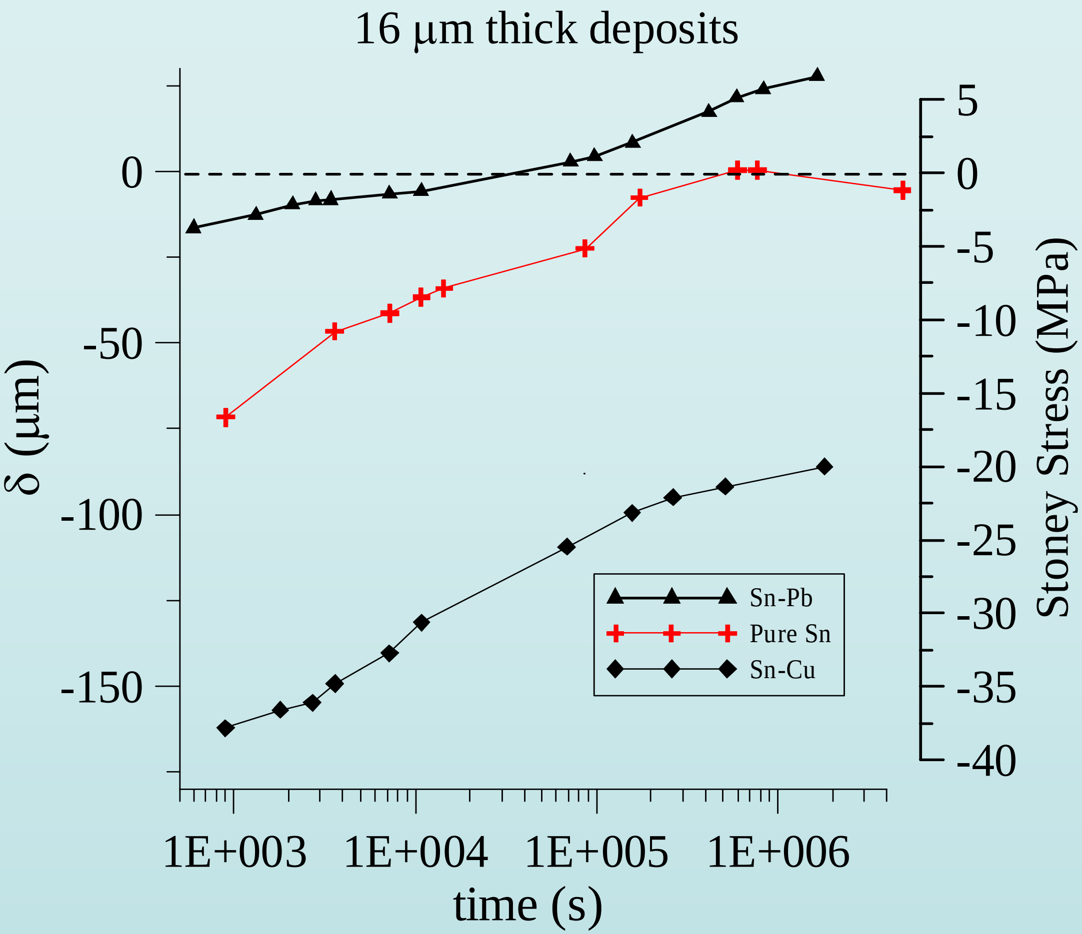

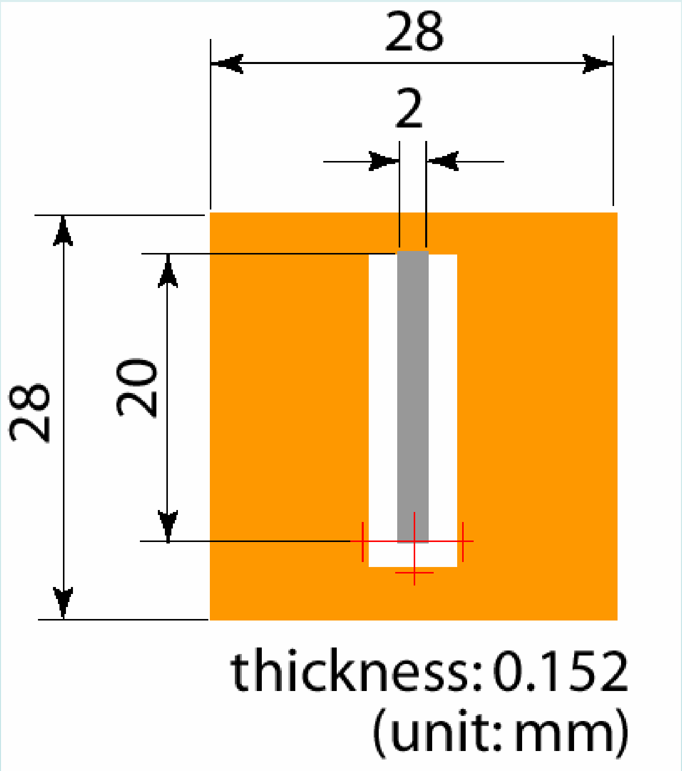

Whisker and hillock formation on Sn, Sn–Cu and Sn–Pb electrodeposits, W.J. Boettinger , C.E. Johnson, L.A. Bendersky, K.-W. Moon, M.E. Williams, G.R. Stafford, Acta Materialia 53 (2005) 5033–5050.

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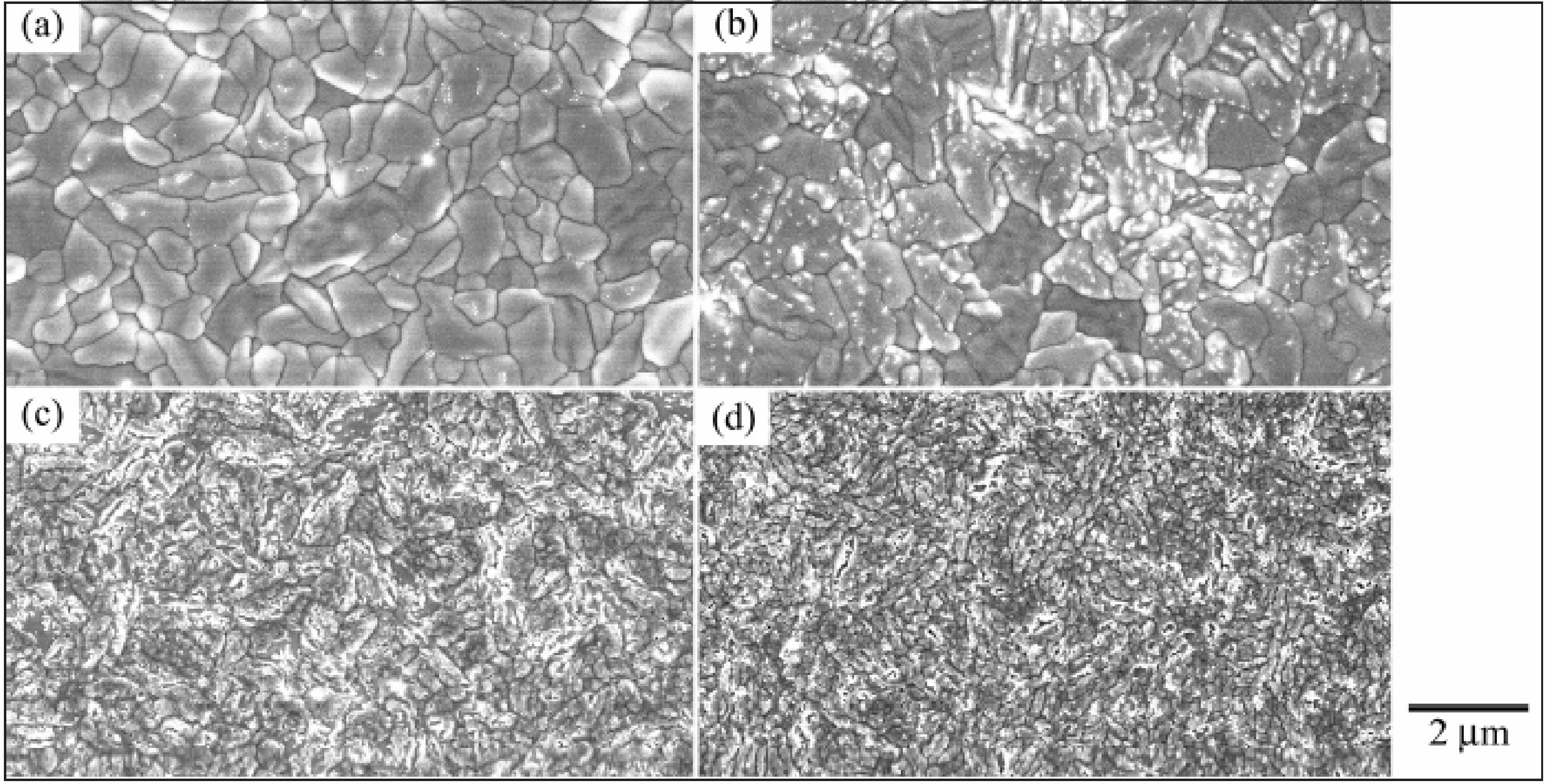

Figure 4. SEM micrographs of the as-deposited surface of 3 µm thick Sn electrodeposits containing (a) 0 %, (b) 1.5 %, (c) 2.9 %, and (d) 3.3 % mass fraction Cu. The substrate was a 250 µm thick Cu deposit from a pyrophosphate electrolyte.

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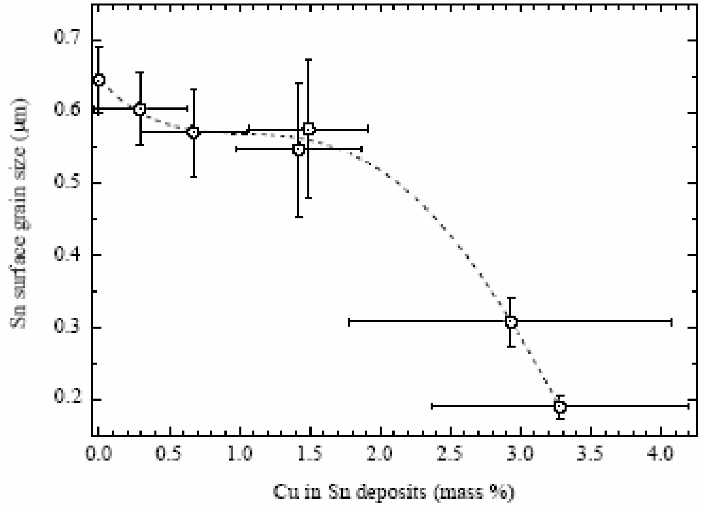
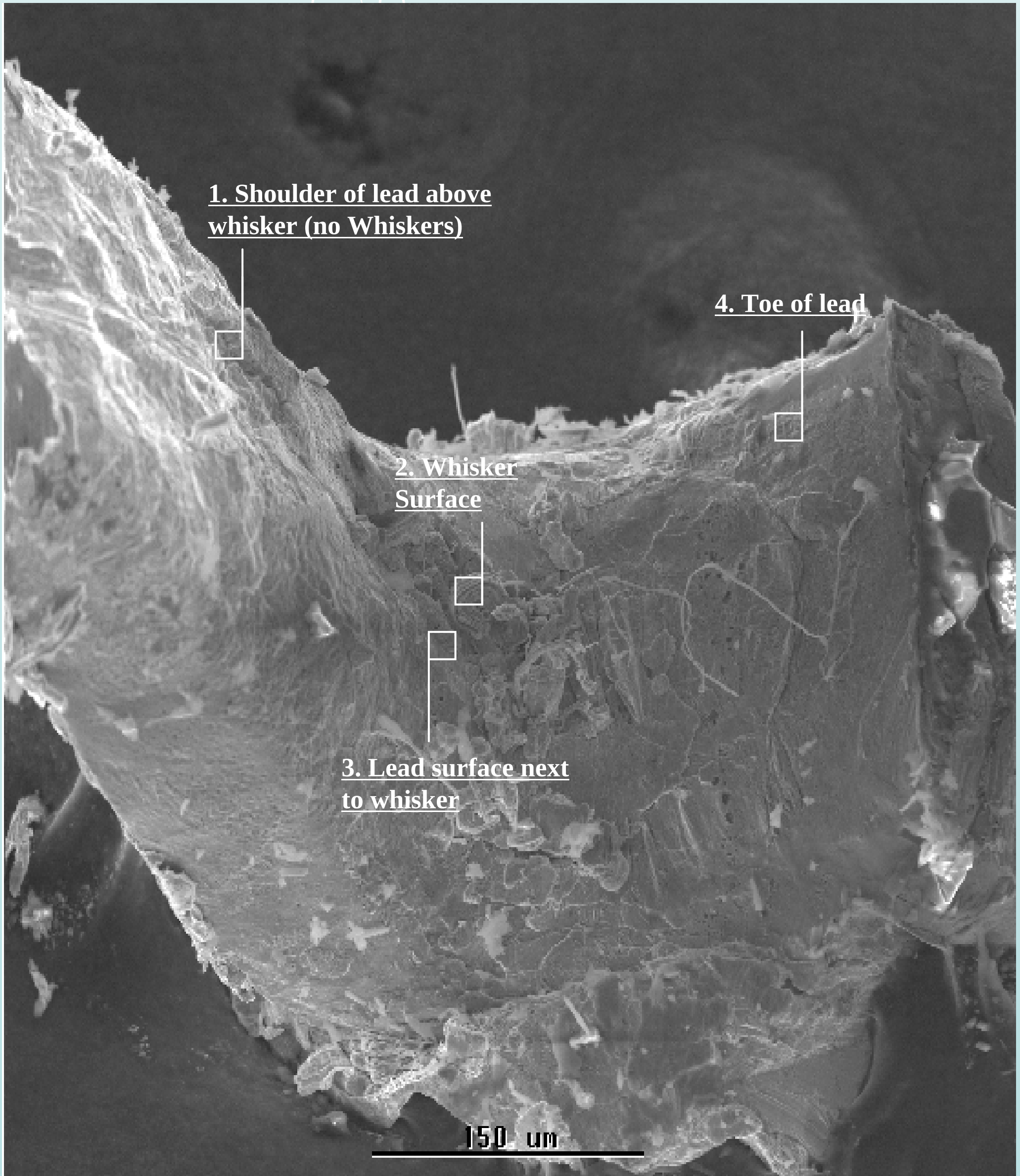


Figure 5. Grain size as a function of Cu content in the Sn-Cu deposit on the pyrophosphate Cu substrate.



	Cl-	WOA-	NH4+	S04-
Shoulder	3.26	5.36	3.62	0.59
Whiskers	14.29	47.14	5.36	3.27
(flux line)				
Toe	7.56	42.31	1.24	2.36
all values are in ug/in2				

The level of ionic contamination on this lead when cut into thirds and analyzed by Ion Chromatography IPC TM-650 2.3.28

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