Effects of Tin and Copper Nanotexturization on Tin Whisker Formation

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The physical mechanisms behind tin whisker formation in pure tin (Sn) films continue to elude the microelectronics industry. Despite modest advances in whisker mitigation techniques (i.e., barrier metal underlayers, substrate/film annealing, etc.) and encapsulation, ways to fundamentally prevent whiskers from forming remain unknown. It has been said that tin plating thicknesses of <0.5 um or >20um are "whisker inhibiting"[3,6]. In the case of the former claim, it may be argued that as film grains approach an equiaxed proportion (i.e., the average columnar grain height is roughly equivalent to the average grain diameter), stress compensation is no longer preferential to the normal direction with respect to the plated film. Grain morphology has often been pointed to in the literature as a likely factor in Sn whisker formation due to the fact that SnPb, which does not whisker, has equiaxed grains while pure Sn exhibits columnar grain growth, which is only equiaxed when the film thickness matches the average grain diameter. Our work examines the effect of adding grain refiners during tin electroplating, with particular focus on the 'as-deposited' film morphology and the associated incidence of whiskering. We have included polycrystalline Sn 'control samples' in our study, and as an extension of our previous work[1], we have compared the structure and whiskering incidence of nanotexturized Sn on both polycrystalline and nanocrystalline Cu underlayers.

Introduction

The availability of conventional eutectic tin-lead solder parts continues to wane in the increasingly ROHS-compliant electronics industry. Given this widespread removal of lead from electronic systems, there is a correspondingly widespread potential risk of failure due to tin whiskers.

Tin whiskers are micro-scale metal filaments that emerge unpredictably from pure tin surfaces as either needle-like filaments, or as extensions of 'odd shaped eruptions' [9] or nodule-like 'hillocks'. They are single-crystalline and conductive, and can grow to significant lengths (>2.0mm) [10], thus creating the potential for electrical shorts between closely spaced leads, traces and solder joints.

It is widely believed that the morphology of Sn films and their underlying substrates (including, but not limited to, the Cu_6Sn_5 intermetallic compound which forms at the interface between Sn and Cu) may play a meaningful role in whisker development, along with stress conditions and/or stress gradients, and possibly environmental conditions. The scientific community remains active in its efforts to uncover the root physics of tin whisker formation [2-5], while others have focused on developing whisker mitigating strategies to cope with the unpredictability of pure Sn [6,8] and to improve the reliability of assemblies in which it is used. In keeping with the latter objective, this paper expands on our previous work, in which mixed whisker mitigation results were obtained in polycrystalline Sn on nanocrystalline and polycrystalline copper after 1000 thermal cycles [1].

Background

The objective of this study was to expand upon our previous work[1], which explored the impact of nanocrystalline copper underlayers on traditional tin plated finishes, and the level of whiskering that resulted. In our previous study, nanocopper was generally found to *reduce* whisker density when the subsequently deposited tin was applied through electron-beam evaporation (a physical vapor deposition (PVD) technique) or bright electroplating. Whiskers were eliminated entirely when bright polycrystalline tin was electroplated on copper deposits with an average grain size of 100nm[1].

In the present work, pure tin films were electrodeposited, using matte and bright electroplating, onto nanocrystalline and polycrystalline copper-clad substrates. Variables explored include plating duty cycle and the amount of grain refining additive introduced. The samples were subjected to thermal cycling conditions in hopes of promoting whisker growth in susceptible samples. The resultant surface morphologies, stress levels, and degree of whiskering are reported.

The deposition of nanostructured deposits is generally accomplished by employing pulsed electro deposition (PED) rectification and with the addition of organic additives such as complex formers and inhibitors to achieve smaller grains. These additives aid in inhibiting crystallite growth, resulting in a finer grained structure. We wish to note that organic additives (i.e., brighteners and antioxidants) did not impact whisker propensity in our previous work, as evidenced by the fact

that our PVD films (ostensibly "pure") whiskered readily, hence we felt comfortable exploring the use of additives for whisker mitigation.

Experimental Detail

Copper Deposition & Analysis
The test substrates used in this study were 1"x1"x 0.010" copper substrates. Nanocrystalline copper deposits were produced with PED rectification in a copper plating bath consisting of copper sulfate, ammonium sulfate and citric acid as a grain refining additive. The deposits were electroplated using a current density of $0.165A/in^2$ at a peak current of 10A. Polycrystalline copper deposits were produced from a standard copper sulfate process using DC rectification. The copper deposits were plated to a thickness of 5 microns.

Scanning Electron Microscopy (SEM) micrographs of the polycrystalline and nanocrystalline copper deposit morphologies are provided in Figures 1a and 1b, respectively. The average grain size of the polycrystalline copper is 2μm, while the average grain size of the nanocrystalline copper is 100nm.
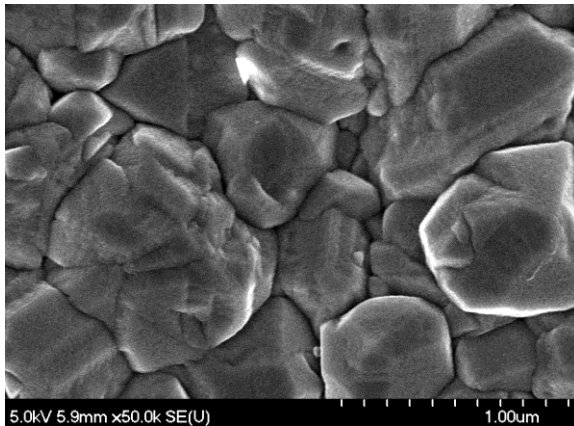

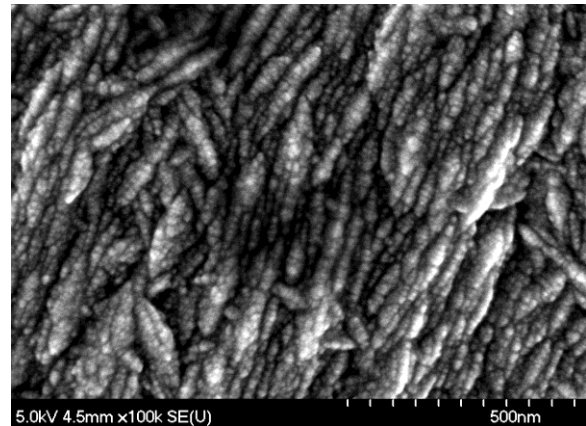**Figure 1a: Polycrystalline Copper Surface (50,000X)**

Figure 1b: Nanocrystalline Copper Surface (100,000X)

Tin Deposition
Pure tin was deposited onto polycrystalline and nanocrystalline copper substrates using matte and bright electroplating with the addition of a grain refiner. A current density of $0.170A/in^2$ was employed, at a peak current of 10A, with various duty cycles. Pure tin anodes were used, with an operating temperature of 25°C and continuous mechanical agitation. Control substrates for the matte and bright tin (listed in Tables 1-2 as BC and MC) were deposited with DC rectification and without a grain refiner for comparison purposes. The process parameters for bright and matte samples are reported in Tables 1 and 2, respectively.

Table 1: Experimental Log of Bright Tin Plating Runs

Index	Sample	Substrate	ON (ms)	OFF (ms)	Additive (grams/L)	Amp*Min
		Bright Tin - Plated to a thickness of 2μm at 0.170 A, 1.4 A*min on 1"x1" copper-clad substrates				
1	BC	polycrystalline copper	DC	DC	none	1.4
2	BC-N	"nano" copper	DC	DC	none	1.4
3	B1	polycrystalline copper	0.1	0.9	50	1.4
4	B1-N	"nano" copper	0.1	0.9	50	1.4
5	B2	polycrystalline copper	1	9	50	1.4
6	B2-N	"nano" copper	1	9	50	1.4
7	B3	polycrystalline copper	1	50	50	1.4
8	B3-N	"nano" copper	1	50	50	1.4
9	B4	polycrystalline copper	0.1	0.9	100	1.4
10	B4-N	"nano" copper	0.1	0.9	100	1.4
11	B5	polycrystalline copper	1	9	100	1.4
12	B5-N	"nano" copper	1	9	100	1.4
13	B6	polycrystalline copper	1	50	100	1.4
14	B6-N	"nano" copper	1	50	100	1.4

Table 2: Experimental Log of Matte Tin Plating Runs

| Index	Sample	Substrate	ON (ms)	OFF (ms)	Additive (grams/L)	Amp*Min
		Matte Tin - Plated to a thickness of 2μm at 0.170 A, 1.4 A*min on 1"x1" copper-clad substrates				
15	MC	polycrystalline copper	DC	DC	none	0.7
16	MC-N	"nano" copper	DC	DC	none	0.7
17	M1	polycrystalline copper	0.1	0.9	50	0.7
18	M1-N	"nano" copper	0.1	0.9	50	0.7
19	M2	polycrystalline copper	1	9	50	0.7
20	M2-N	"nano" copper	1	9	50	0.7
21	M3	polycrystalline copper	1	50	50	0.7
22	M3-N	"nano" copper	1	50	50	0.7
23	M4	polycrystalline copper	0.1	0.9	100	0.7
24	M4-N	"nano" copper	0.1	0.9	100	0.7
25	M5	polycrystalline copper	1	9	100	0.7
26	M5-N	"nano" copper	1	9	100	0.7
27	M6	polycrystalline copper	1	50	100	0.7
28	M6-N	"nano" copper	1	50	100	0.7

As explained in our previous study, we selected a tin thickness of 2 microns, since it falls between 20 μm, the upper whisker-mitigating threshold, and 1 μm, the lower whisker-mitigating threshold, as suggested by Ostermann [6], but also because it is the lower-threshold, below which whisker growth is, also retarded [3].

Thermal Cycling
After tin deposition, all samples were subjected to thermal cycling in accordance with IEC60068-2-82. The temperature range was -55°C to +85°C, with 10min dwells, over the course of 9 days.

Figure 2a: Bright Polycrystalline Tin on Nanocrystalline Copper – Control Sample (Index 2)
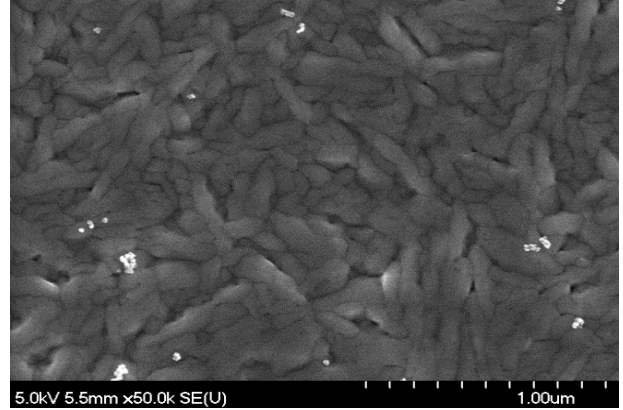
Figure 2b: Bright, Grain Refined Tin on Nanocrystalline Copper (pulsed 0.1ms:0.9ms) (Index 4)
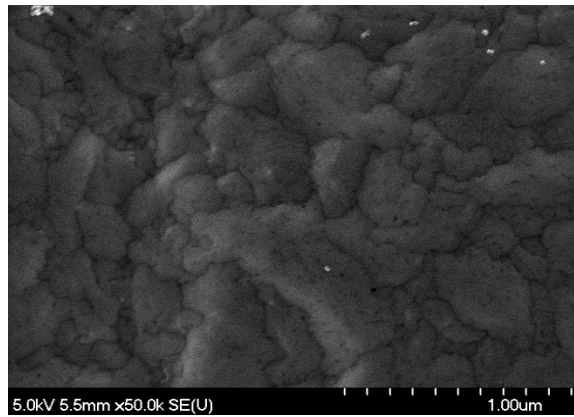
Figure 2c: Bright, Grain Refined Tin on Nanocrystalline Copper (pulsed 1ms:9ms) (Index 6)

Microanalysis
Analysis was performed using scanning electron microscopy (SEM) once all cycles were completed. A series of micrographs showing the tin morphology from "control" (polycrystalline) through varying degrees of grain refinement is presented in Figures 2a-2c (for bright films) and Figure 3a-3c (for matte films).
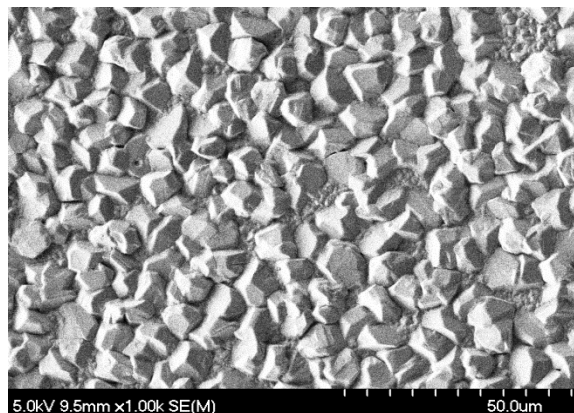

Figure 3a: Matte Polycrystalline Tin on Nanocrystalline Copper – Control Sample (Index 16)
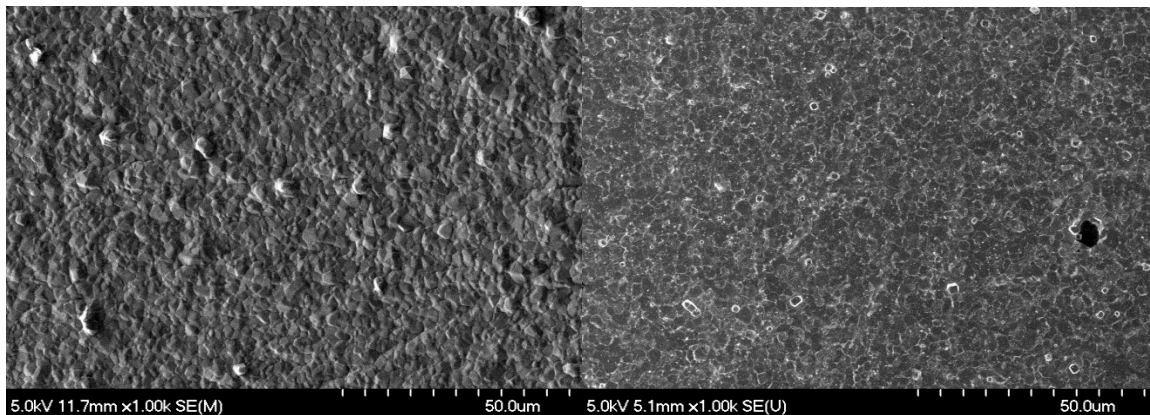
Figure 3b: Matte, Grain Refined Tin on Nanocrystalline Copper (pulsed 0.1ms:0.9ms) (Index 18)

Figure 3c: Matte, Grain Refined Tin on Nanocrystalline Copper (pulsed 1ms:9ms) (Index 20)

In the case of bright tin on nanocrystalline copper, there is a clear evolution from distinct, oblong grains to an increasingly coalesced appearance, with a linear decrease in average surface roughness. In the case of matte tin on nanocrystalline copper, there is a nonlinear progression in roughness, but a clear 'smoothing' has taken place for both grain-refined samples, with respect to the polycrystalline control.
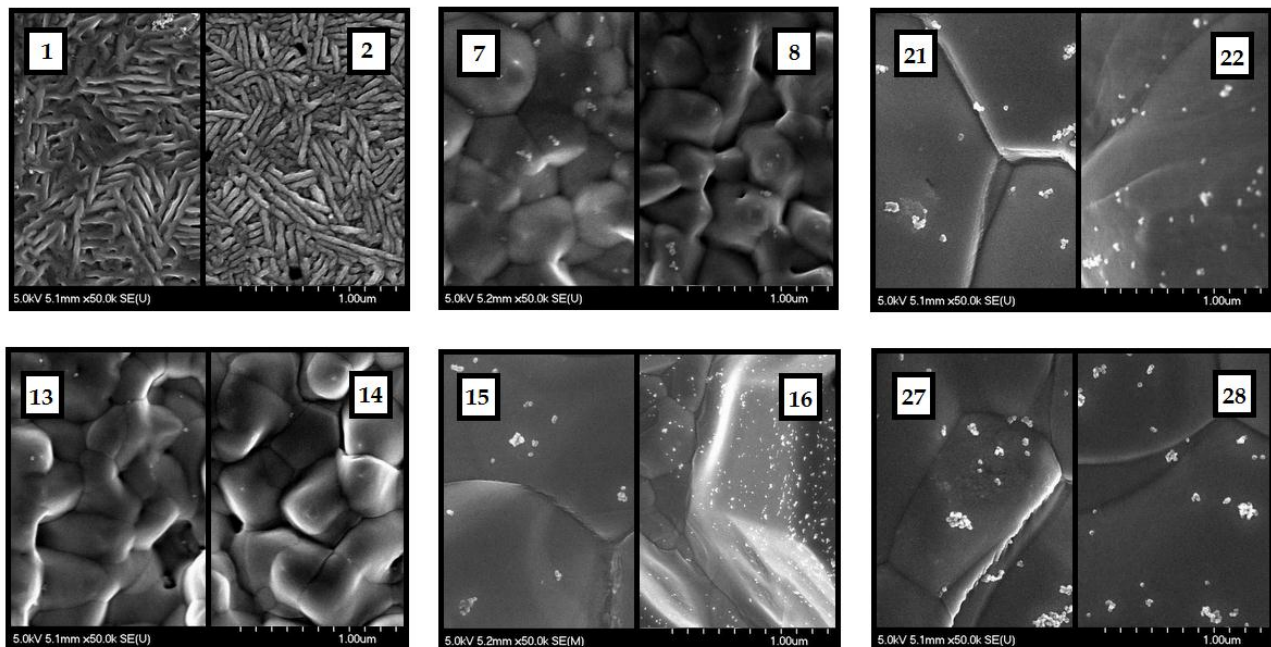
Figure 4: Side-by-side comparisons of identical tin films atop polycrystalline copper underlayers (left-hand side of image) and atop Nanocrystalline copper underlayers (right-hand side of image). Numbers correspond to indices listed in Tables 1 and 2 above.

Side-by-side comparisons of tin films atop polycrystalline vs. Nanocrystalline copper underlayers are presented in Figure 4. The morphology of the underlying copper does not appear to have imparted any change in the observed surface texture of the plated tin, for any formulation applied.

Stress and Surface Roughness

The surface roughnesses of eight different types of tin, named IPC-1 through IPC-8 (summarized in Table 3 below), were measured using a Veeco Wyko NT1100 Optical Profiler System at 50X magnification, 1374 frames per image. We also measured the as-deposited stresses in IPC1-IPC8 using a laser-based KLA Tencor FLX Film Stress Measurement System. The test substrates for stress and surface roughness measurements consisted of 4 inch round silicon wafers which had been metallized with 300 Å of chromium and 1µm of copper (as seed layer) using electron beam evaporation, followed by 2 microns of electroplated tin (per Table 3, samples IPC1-IPC8). The radii of curvature and bow were measured after the seed evaporation step (for background), and then again after electroplating to get a comparative stress reading.

The data in Table 4 show that the Nanocrystalline deposit stress does not differ significantly or linearly in magnitude with respect to the polycrystalline copper deposits. The surface roughnesses of IPC2 and IPC3 (both nanocrystalline matte) are smaller than that of IPC1 (polycrystalline matte), while IPC4 (nanocrystalline matte) is slightly larger. IPC 7 and IPC8 (both Nanocrystalline bright), on the other hand, both have larger surface roughnesses with respect to IPC5 (polycrystalline bright), while IPC6 (also Nanocrystalline bright) is smaller.
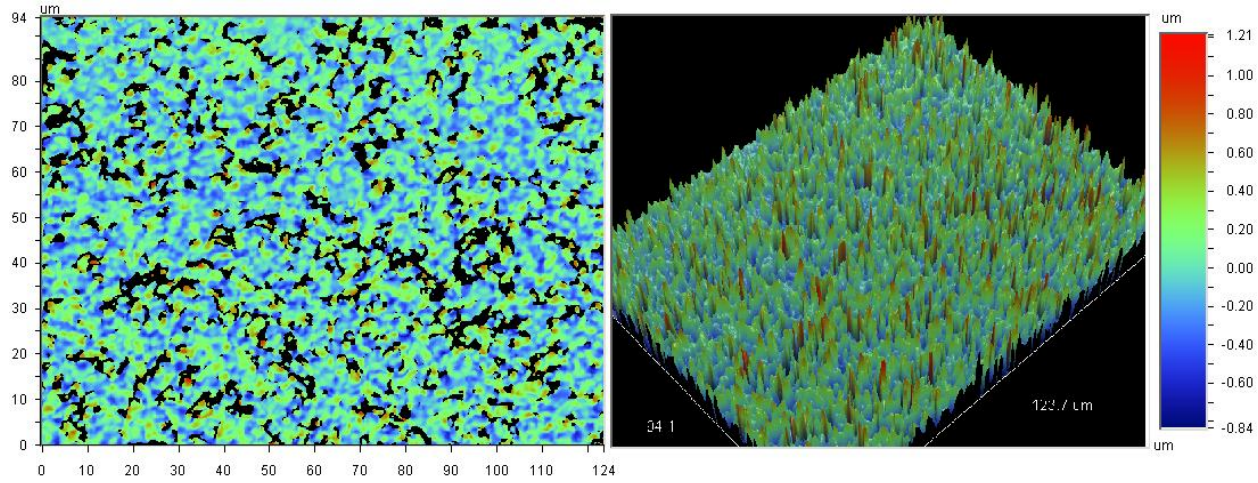
Figure 5: Optical Profilometry Scans of Surface Roughness, Plan (left) and 3-D (right) views, Sample IPC2

**Table 3: Deposition Parameters for IPC1-IPC8**

Matte Tin - Plated to a thickness of 2μm on 4" round substrates with nanocrystalline copper underlayer

Sample	ON (ms)	OFF (ms)	Current (A)	Additive (grams)	Amp*Min
IPC-1	DC	DC	0.581	none	2.4
IPC-2	0.1	0.9	0.581	200	2.4
IPC-3	1	9	0.581	200	2.4
IPC-4	1	50	0.17	200	2.4

Bright Tin - Plated to a thickness of 2μm on 4" round substrates with nanocrystalline copper underlayer

Sample	ON (ms)	OFF (ms)	Current (A)	Additive (grams)	Amp*Min
IPC-5	DC	DC	0.581	none	4.8
IPC-6	0.1	0.9	0.581	100	4.8
IPC-7	1	9	0.581	100	4.8
IPC-8	1	50	0.581	100	4.8

Table 4: Surface Roughness and Stress for IPC1

| Sample	Surface Roughness (nm)	Stress (Mpa tensile)	Radius of Curvature (m)
IPC1	209	too rough	N/A
IPC2	186.36	16.7	86.96
IPC3	153.59	13.9	150.916
IPC4	218.31	12.3	-355.695
IPC5	35.27	13.8	104.73
IPC6	31	26.7	90.853
IPC7	64.36	15.6	48.978
IPC8	142.93	too rough	N/A

Tin Whiskering

Of the 14 bright tin samples prepared using a nanocopper underlayer, only three showed evidence of whiskering (Indices 4, 6, and 10). A variety of whisker morphologies were observed, including the classical striated needle-like filaments, odd-shaped eruptions, hillocks, and smooth, rectangular-shaped growths. Figure 6 shows a hillock (which may eventually evolve into a whisker after aging) formed in the surface of the bright control sample (Index 2), and Figure 7 shows rectangular whiskers formed in the surface of the matte control sample (Index 16). In disagreement with our previous work [1], we found that matte polycrystalline tin on polycrystalline copper *did* form whiskers (Figure 8), while matte tin on *nano*crystalline copper *did not* form whiskers (Figure 3a). Further aging under ambient conditions is planned over the course of the next year, and new inspections will then be performed to gauge the differences in whiskering level for all samples.
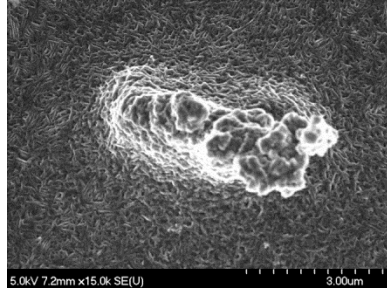
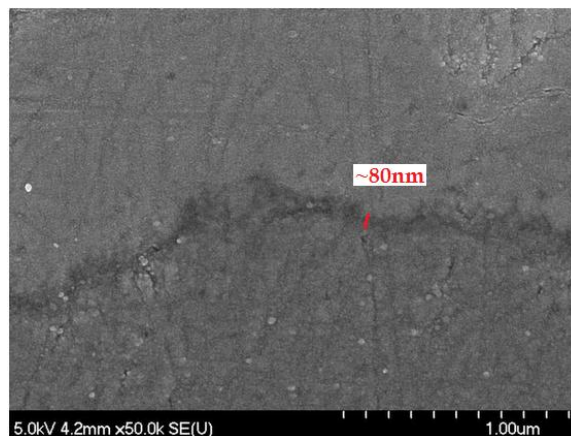**Figure 6: Hillock in Bright Polycrystalline Tin on Nanocrystalline Copper - Control Sample (Index 2)**
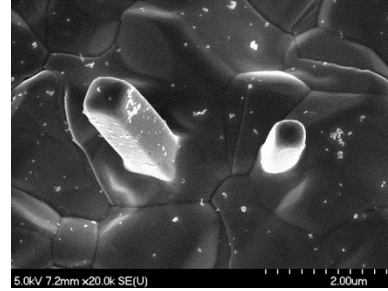
Figure 7: "Rectangular" Whiskers in Matte Polycrystalline Tin on Polycrystalline Copper Control Sample (Index 15)
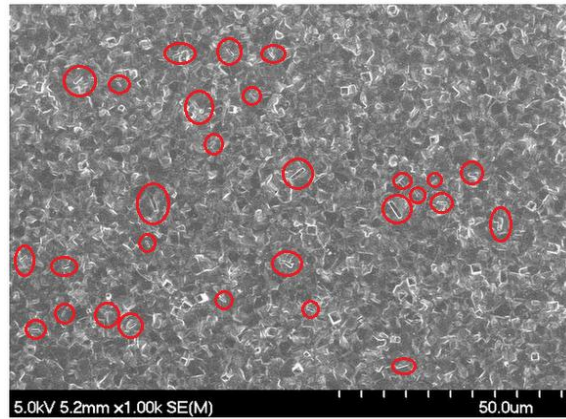

Figure 8: Surface of Matte Polycrystalline Tin on Polycrystalline Copper (Index 15) - Whiskered

Intermetallic Compound Measurement

After the collection of plan-view SEM micrographs was completed, four samples were potted and cross-sectioned. The tin-copper interface and intermetallic compound (IMC) region was imaged twice: once after mechanical polishing (Figures 9-12) and once following a 2-minute wet chemical etch using a commercial Sn stripper (Figures 13-16). The meandering demarcation line is clearly visible prior to etching, and thickness estimates are provided. The IMC volume is visibly larger, in terms of volume and thickness, in the case of Grain Refined Tin for both matte and bright samples, when compared with the polycrystalline tin versions.
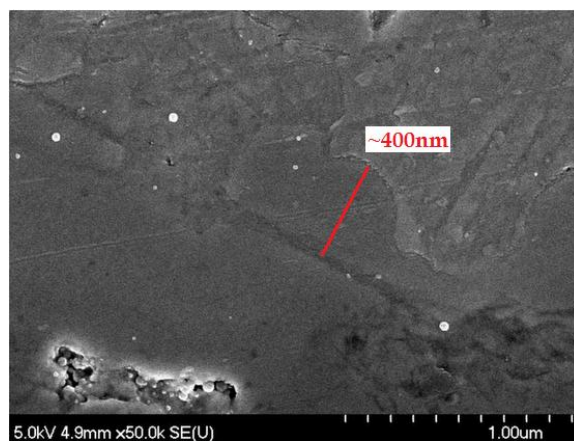

Figure 9: Matte Polycrystalline Tin on Nanocrystalline Copper – Control Sample (Index 16)
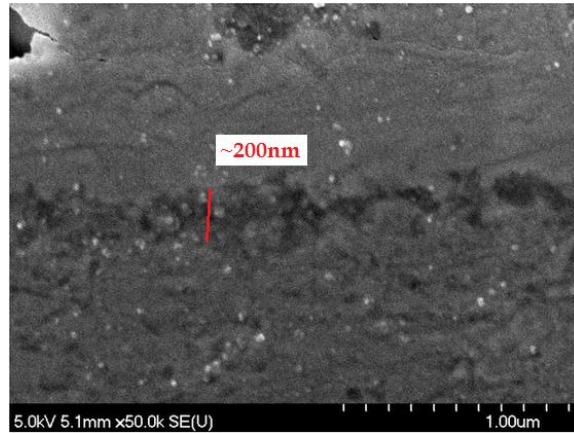
Figure 10: Matte, Grain Refined Tin on Nanocrystalline Copper (pulsed 1ms:50ms) (Index 28)
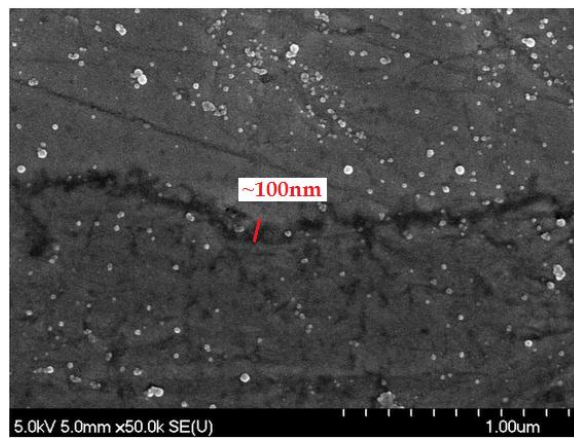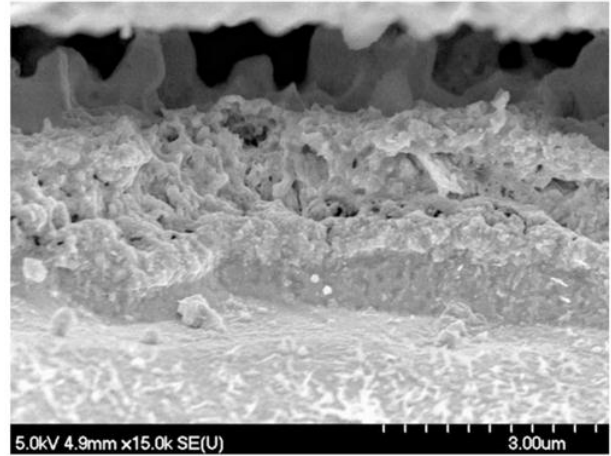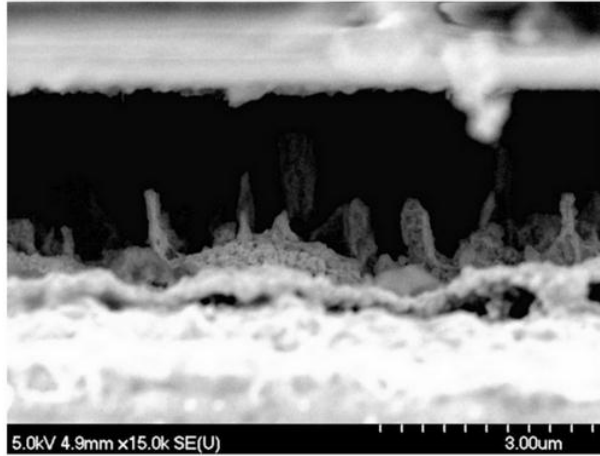

Figure 11: Bright Polycrystalline Tin on Nanocrystalline Copper - Control Sample (Index 2)
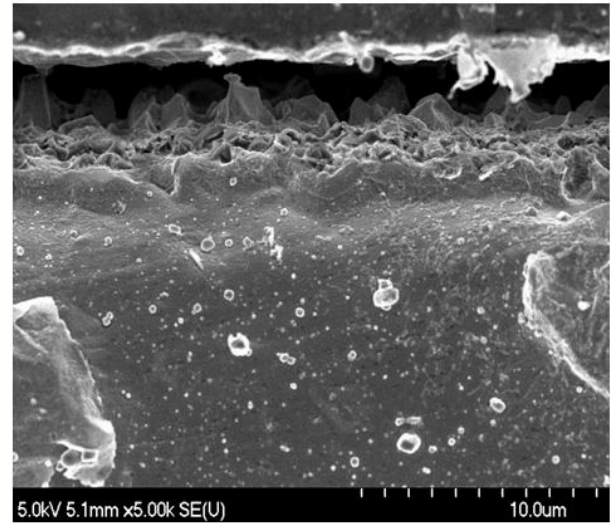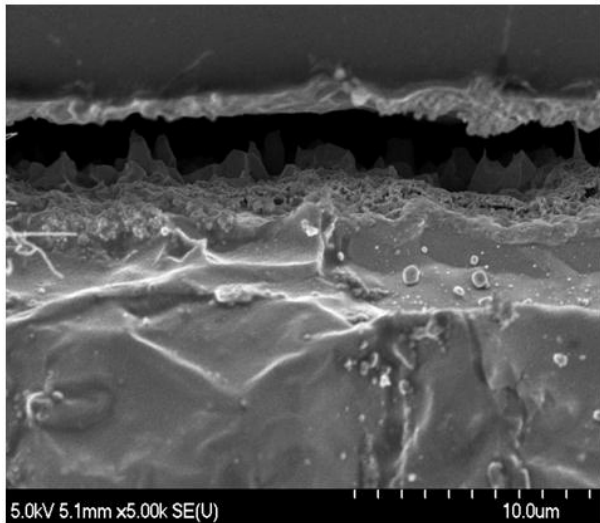

Figure 12: Bright, Grain Refined Tin on Nanocrystalline Copper (pulsed 1ms:50ms) (Index 14)

Figure 13(left) and 14(right): Intermetallic grains are visible within the etched gap between the copper substrate/seed layer and the epoxy encapsulant. Figure 13 depicts bright polycrystalline tin on nanocopper, while Figure 14 depicts bright nanocrystalline tin on nanocopper.

Figure 15(left) and 16(right): Intermetallic grains are visible within the etched gap between the copper substrate/seed layer and the epoxy encapsulant. Figure 13 depicts matte polycrystalline tin on nanocopper, while Figure 14 depicts matte nanocrystalline tin on nanocopper

Conclusions

We have successfully demonstrated the ability to modify the grain size, shape, and texture of tin through pulse plate deposition and the addition of a grain refining additive. Sample cross-sections, pre- and post-etching, may indicate an increased intermetallic compound volume in samples with grain refined tin on nanocrystalline copper. Preliminary imaging suggests that nanocopper underlayers prevent whiskers from forming in polycrystlline tin, while polycrystalline copper underlayers do not – an inversion of our previous finding[1]. Our intent is to conduct ambient aging of all 28 samples over the coming year, and to perform follow-on microscopy analysis to evaluate any differences in whiskering propensity with respect to the degree of nanotexturization and/or surface smoothing.

Lead-free solder is a reality in today's microelectronics industry, and the unpredictable nature of tin whiskers poses a significant challenge to determining microelectronics reliability. Further work is needed (and planned) in determining whether modifying the intrinsic grain morphology of plated filsm can help to redistribute the as-plated and evolutionary stresses and either retard or prevent tin whisker growth from occurring.

References

[1]   D.M. Lee, L.A. Piñol, "Effects of Tin Whisker Formation on Nanocrystalline Copper," *IPC Printed Circuit Expo, APEX & Designer Summit Proceedings*, 2011.

[2]   J. Cheng, P. Vianco, et al., "Nucleation and Growth of Tin Whiskers," *Applied Physics Letters*, 98, 2011.

[3]   T. Kato, H. Akahoshi, et al., "Correlation Between Whisker Initiation and Compressive Stress in Electrodeposited Tin-Copper Coating on Copper Leadframes," *IEEE Transactions on Electronics Packaging Manufacturing*, 33 (3) pp. 165-176, July 2010.

[4]   L. Piñol, "Fundamental Studies of Tin Whiskering in Microelectronics Finishes," University of Maryland College Park PhD Dissertation, College of Electrical & Computer Engineering, May 2010.

[5]   S. Lal, T. Moyer, "Role of Intrinsic Stresses in the Phenomena of Tin Whiskers in Electrical Connectors," *IEEE Transactions on Electronics Packing Manufacturing*, 28 (1) pp. 63-74, 2005.G.T.

[6]   M. Osterman, "Mitigation Strategies for Tin Whiskers," accessed at: http://www.calce.umd.edu/lead-free/tin-whiskers/TINWHISKERMITIGATION.pdf.

[7]   G. Galyon, "Annotated Tin Whisker Bibliography and Anthology," *IEEE Transactions on Electronics Packaging Manufacturing*, 28 (1) pp. 94-122, 2005.

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[9]   W. Woodrow, "Evaluation of Conformal Coatings as a Tin Whisker Mitigation Strategy," *IPC/JEDEC 8th International Conference on Lead-Free Electronic Components and Assemblies*, 2005.

[10]   I. Herneflord, "Tin Whiskers on a Tin-Plated Flange of a Ka Band Waveguide," *NASA Anecdote #2: Tin Whiskers on Waveguide*, accessed at: http://nepp.nasa.gov/whisker/anecdote/2004waveguide/index.html.

David Lee is a Process Engineer for the Johns Hopkins Applied Physics Laboratory. He has twenty eight years' experience working in the microelectronics field. He specializes in plating flight qualified hardware and electronics utilizing electroless and electrolytic plating processes. He was awarded two United States patents for the development of electroless plating processes. He also has an extensive background in processing thin film hybrid microcircuits.

Dr. Lesly A. Piñol is a Senior Staff Microelectronics Engineer at the Johns Hopkins University Applied Physics Laboratory. She received her B.S. and M.S. degrees from Northern Illinois University in 2004 and her PhD from the University of Maryland, College Park in 2010. Her primary areas of interest include tin whisker research, microelectronics process technology, and nanomaterials.

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RoHS Directive

- Widespread conversion to lead-free solder technology
- Exemptions from the directive (military, space, and biomedical agencies)
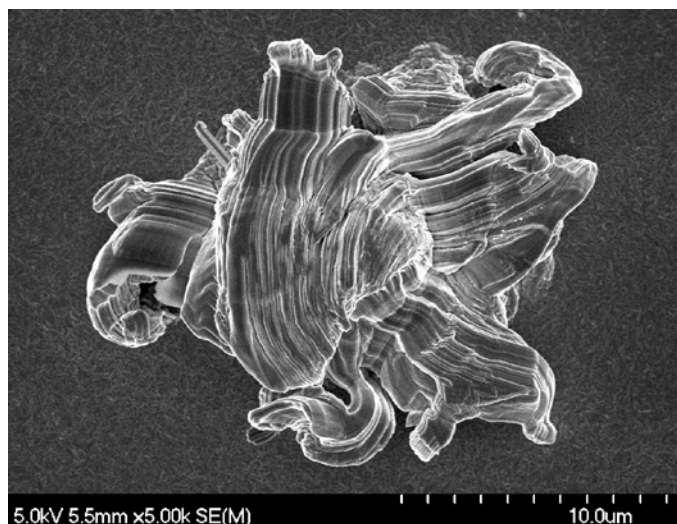- Potential risk of failure due to tin whiskers

Tin Whiskers

- Micro-scale metal filaments that can emerge unpredictably from pure tin surfaces
- Potential for electrical shorts between closely spaced wires and joints
- Conductive and can be greater then 2.0mm long
- Some whiskers grow rapidly (days), others would take months

Examples of Tin Whiskers

'Odd Shaped Eruptions'
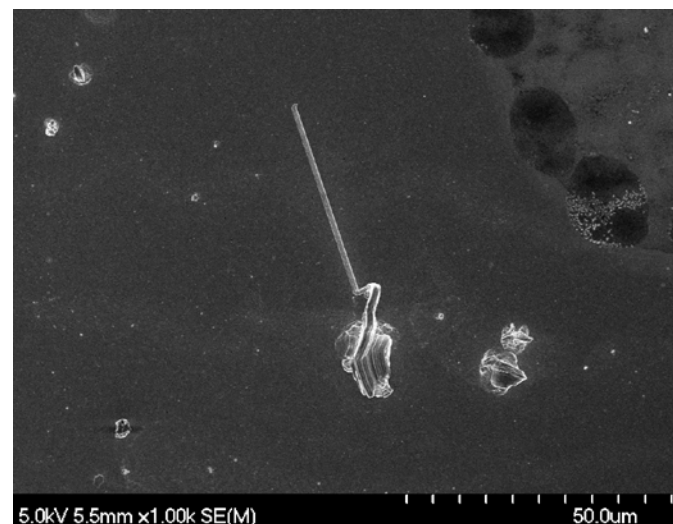
Needle-Like Filaments

Whisker Formation Theories

- The morphology of tin films and their underlying substrates

- Cu_6Sn_5 intermetallic compound which forms at the interface between Sn and Cu

- Stress conditions and/or stress gradients

- Environmental conditions

Previous Whisker Mitigating Study

- Studied the impact of nanocrystalline copper underlayers on traditional tin plated finishes

- Polycrystalline tin was deposited on nanocrystalline and polycrystalline copper.

- Nanocrystalline copper was generally found to reduce whisker density when the subsequently deposited tin was applied through electron-beam evaporation (a physical vapor deposition (PVD) technique) or bright electroplating.

Objectives of Follow-On Study

- Compare the structure and whiskering incidence of nanotexturized tin on both polycrystalline and nanocrystalline copper underlayers.

- Examine the effect of the addition of grain refiners to the tin electroplating process.

- Produce tin deposits with pulsed electro deposition (PED) rectification.

- Subject tin deposits to thermal cycling conditions in hopes of promoting whisker growth in susceptible samples.

- Report the resultant surface morphologies, stress levels, and degree of whiskering.
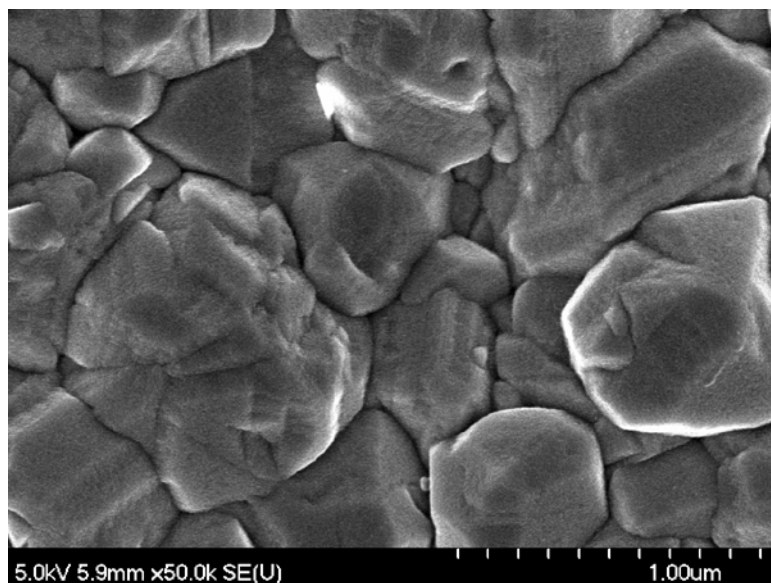
Experimental Detail
Copper Underlayer

- Test coupons used were 1"x1"x 0.010" copper substrates.

- Nanocrystalline copper deposits with an average grain size of 100nm were produced with PED rectification and citric acid as a grain refining additive.

- Polycrystalline copper deposits with an average grain size of about 2 microns were produced from a standard copper plating process using DC rectification.

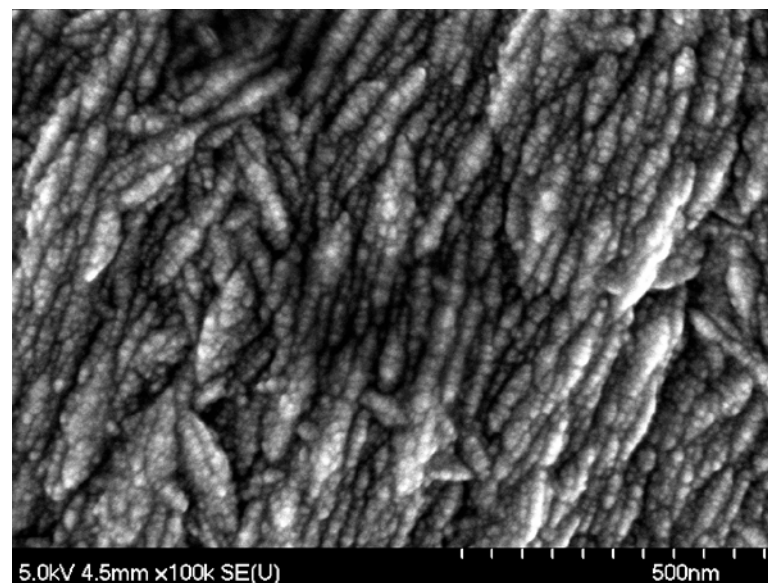- The deposits were plated to a thickness of 5 microns.

Copper Underlayers

Polycrystalline Copper
Average Grain Size: 2μm

Nanocrystalline Copper
Average Grain Size: 100nm

Experimental Detail
Tin Deposition

- Matte and bright tin deposits with various grain sizes were electroplated onto the polycrystalline and nanocrystalline copper substrates.

- The tin deposits were electroplated using a current density of $0.170A/in^2$ at a peak current of 10A.

- Pure tin anodes were used at an operating temperature of 25ºC with mechanical agitation

- Variables explored were plating duty cycle and the amount of grain refining additive introduced.

- A thickness of 2 microns was selected, a value which falls between 20 µm (upper whisker-mitigating threshold) and 1 µm (lower whisker-mitigating threshold).

Bright Tin Deposition

			ON (ms)	OFF (ms)	Additive (grams/L)	Amp*Min
Index	**Sample**	**Substrate**				

<table>
<tr><td colspan="7" align="center">Bright Tin - Plated to a thickness of 2μm at 0.170 A, 1.4 A*min
on 1"x1" copper-clad substrates</td></tr>
<tr><td>Index</td><td>Sample</td><td>Substrate</td><td>ON (ms)</td><td>OFF (ms)</td><td>Additive (grams/L)</td><td>Amp*Min</td></tr>
<tr><td>1</td><td>BC</td><td>polycrystalline copper</td><td>DC</td><td>DC</td><td>none</td><td>1.4</td></tr>
<tr><td>2</td><td>BC-N</td><td>"nano" copper</td><td>DC</td><td>DC</td><td>none</td><td>1.4</td></tr>
<tr><td>3</td><td>B1</td><td>polycrystalline copper</td><td>0.1</td><td>0.9</td><td>50</td><td>1.4</td></tr>
<tr><td>4</td><td>B1-N</td><td>"nano" copper</td><td>0.1</td><td>0.9</td><td>50</td><td>1.4</td></tr>
<tr><td>5</td><td>B2</td><td>polycrystalline copper</td><td>1</td><td>9</td><td>50</td><td>1.4</td></tr>
<tr><td>6</td><td>B2-N</td><td>"nano" copper</td><td>1</td><td>9</td><td>50</td><td>1.4</td></tr>
<tr><td>7</td><td>B3</td><td>polycrystalline copper</td><td>1</td><td>50</td><td>50</td><td>1.4</td></tr>
<tr><td>8</td><td>B3-N</td><td>"nano" copper</td><td>1</td><td>50</td><td>50</td><td>1.4</td></tr>
<tr><td>9</td><td>B4</td><td>polycrystalline copper</td><td>0.1</td><td>0.9</td><td>100</td><td>1.4</td></tr>
<tr><td>10</td><td>B4-N</td><td>"nano" copper</td><td>0.1</td><td>0.9</td><td>100</td><td>1.4</td></tr>
<tr><td>11</td><td>B5</td><td>polycrystalline copper</td><td>1</td><td>9</td><td>100</td><td>1.4</td></tr>
<tr><td>12</td><td>B5-N</td><td>"nano" copper</td><td>1</td><td>9</td><td>100</td><td>1.4</td></tr>
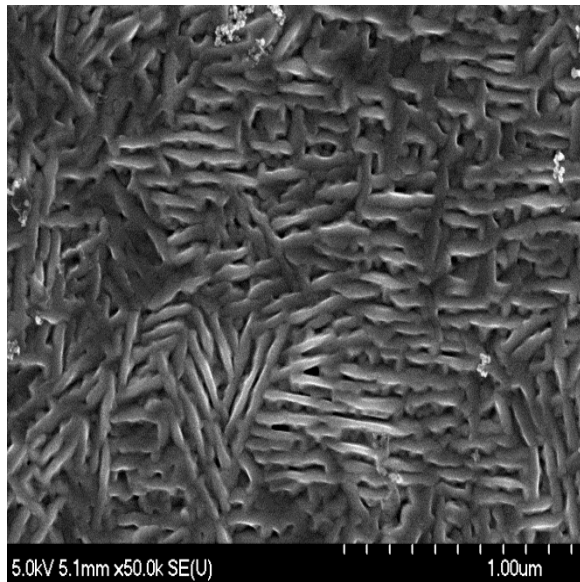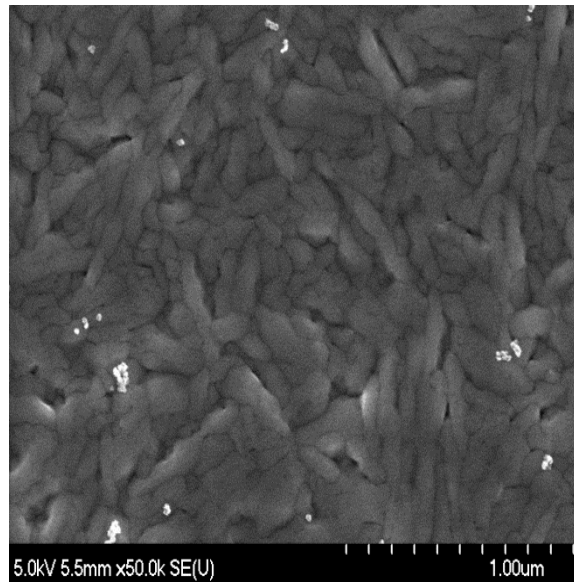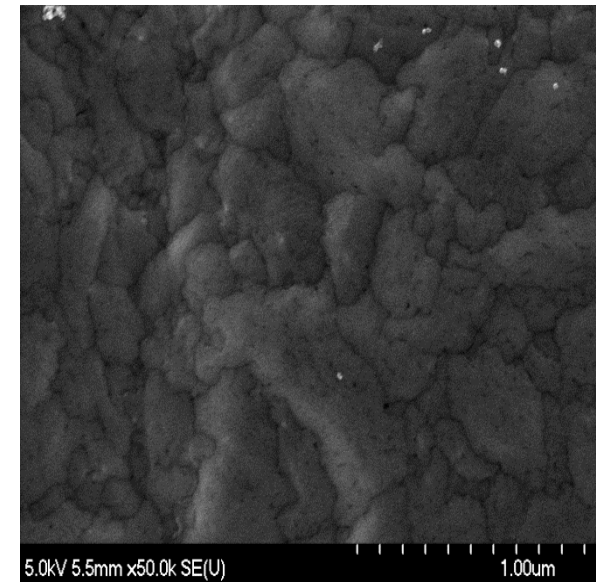<tr><td>13</td><td>B6</td><td>polycrystalline copper</td><td>1</td><td>50</td><td>100</td><td>1.4</td></tr>
<tr><td>14</td><td>B6-N</td><td>"nano" copper</td><td>1</td><td>50</td><td>100</td><td>1.4</td></tr>
</table>

Matte Tin Deposition

Matte Tin - Plated to a thickness of 2μm at 0.170 A, 1.4 A*min on 1"x1" copper-clad substrates						
Index	**Sample**	**Substrate**	**ON (ms)**	**OFF (ms)**	**Additive (grams/L)**	**Amp*Min**
15	MC	polycrystalline copper	DC	DC	none	0.7
16	MC-N	"nano" copper	DC	DC	none	0.7
17	M1	polycrystalline copper	0.1	0.9	50	0.7
18	M1-N	"nano" copper	0.1	0.9	50	0.7
19	M2	polycrystalline copper	1	9	50	0.7
20	M2-N	"nano" copper	1	9	50	0.7
21	M3	polycrystalline copper	1	50	50	0.7
22	M3-N	"nano" copper	1	50	50	0.7
23	M4	polycrystalline copper	0.1	0.9	100	0.7
24	M4-N	"nano" copper	0.1	0.9	100	0.7
25	M5	polycrystalline copper	1	9	100	0.7
26	M5-N	"nano" copper	1	9	100	0.7
27	M6	polycrystalline copper	1	50	100	0.7
28	M6-N	"nano" copper	1	50	100	0.7

Bright Tin Deposits

**Bright Polycrystalline Tin on
Nanocrystalline Copper**
(Control Sample)

**Bright, Grain Refined Tin on
Nanocrystalline Copper**
(pulsed 0.1ms:0.9ms, grain refiner 50g/L)

**Bright, Grain Refined Tin on
Nanocrystalline Copper**
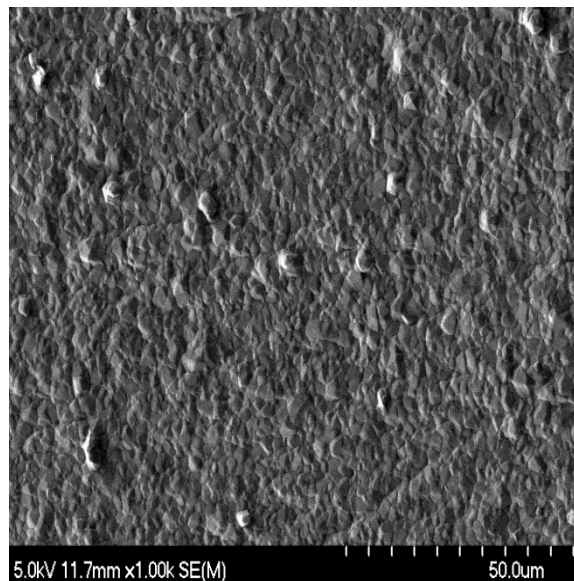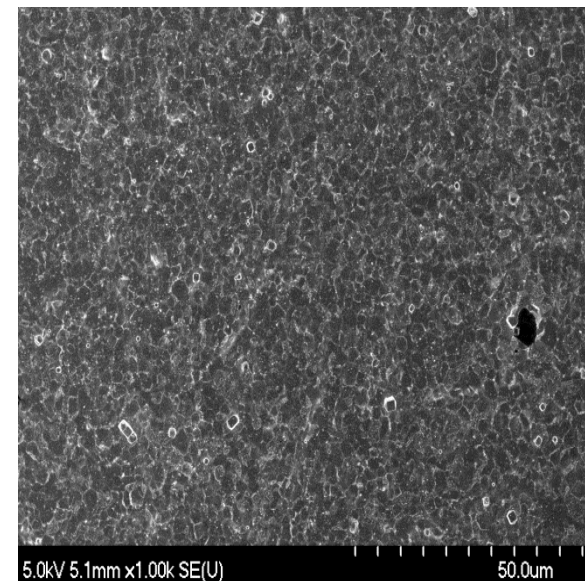**(pulsed 1ms:9ms, grain refiner 50g/L)**

Matte Tin Deposits
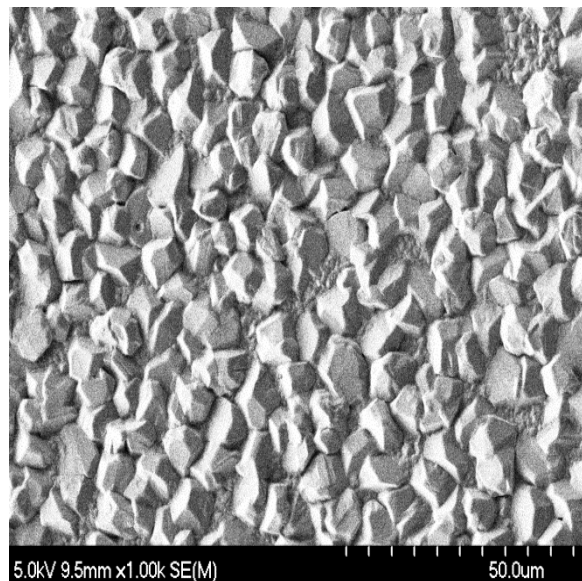
**Matte Polycrystalline Tin on
Nanocrystalline Copper
(Control Sample)**

**Matte, Grain Refined Tin on
Nanocrystalline Copper
(pulsed 0.1ms:0.9ms, grain refiner 100g/L)**

**Matte, Grain Refined Tin on
Nanocrystalline Copper
(pulsed 1ms: 9ms, grain refiner 100g/L)**

Side-by-side Comparisons

Polycrystalline vs. Nanocrystalline Copper Underlayers
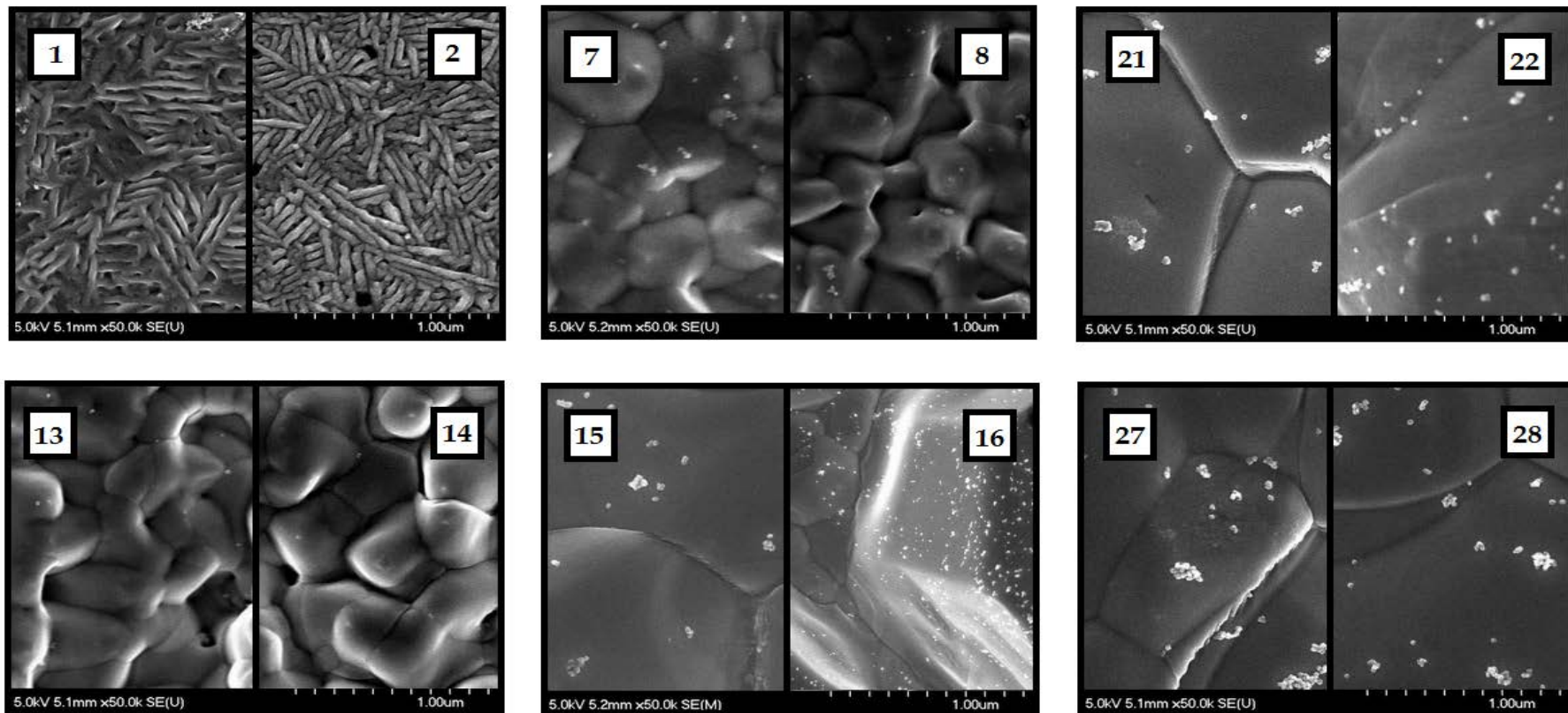
Side-by-side comparisons of identical tin films atop polycrystalline copper underlayers (left-hand side of image) and atop nanocrystalline copper underlayers (right-hand side of image). Numbers correspond to indices listed in Tables 1 and 2

Stress and Surface Roughness

- The test substrates for stress and surface roughness measurements consisted of 4" round silicon wafers which had been metallized with 300 Å of chromium and 1μm of copper (as seed layer) using electron beam evaporation, followed by 2μm of electroplated tin.

- The surface roughnesses of eight different types of tin deposits were measured using a Veeco Wyko NT1100 Optical Profiler System at 50X magnification, 1374 frames per image.

- The as-deposited stresses were measured using a laser-based KLA Tencor FLX Film Stress Measurement System.

Surface Roughness
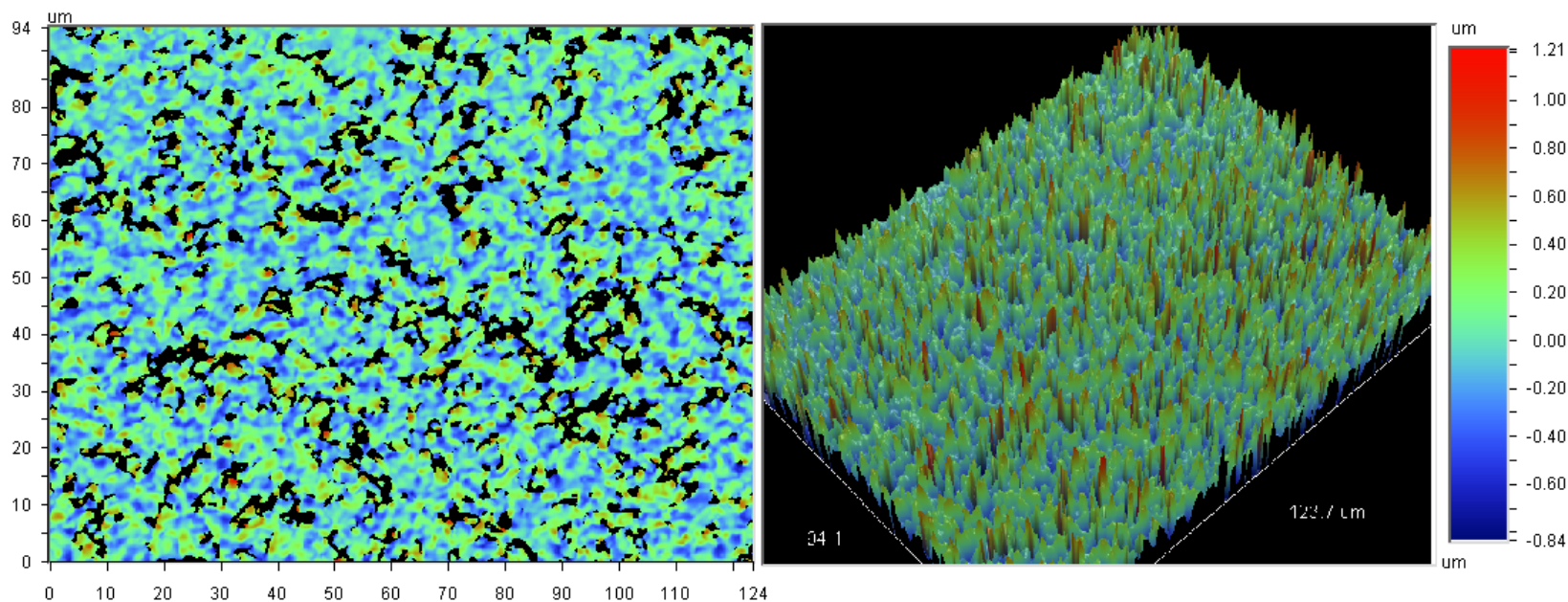
Optical Profilometer Scans of Surface Roughness, Plan (left) and 3-D (right) views, Sample IPC2

Stress and Surface Roughness

Matte Tin - Plated to a thickness of 2μm on 4" round substrates

Sample	Substrate	ON	OFF	Current	Additive	Amp*Min
IPC-1	copper	DC	DC	0.581 A	none	2.4
IPC-2	copper	0.1	0.9	0.581 A	200 grams	2.4
IPC-3	copper	1	9	0.581 A	200 grams	2.4
IPC-4	copper	1	50	0.170 A	200 grams	2.4

Bright Tin - Plated to a thickness of 2μm on 4" round substrates

Sample	Substrate	ON	OFF	Current	Additive	Amp*Min
IPC-5	copper	DC	DC	0.581 A	none	4.8
IPC-6	copper	0.1	0.9	0.581 A	100 grams	4.8
IPC-7	copper	1	8	0.581 A	100 grams	4.8
IPC-8	copper	1	50	0.581 A	100 grams	4.8

Sample	Surface Roughness (nm)	Stress (Mpa tensile)	Radius of Curvature (m)
IPC1	209	too rough	N/A
IPC2	186.36	16.7	86.96
IPC3	153.59	13.9	150.916
IPC4	218.31	12.3	-355.695
IPC5	35.27	13.8	104.73
IPC6	31	26.7	90.853
IPC7	64.36	15.6	48.978
IPC8	142.93	too rough	N/A

Thermal Cycling

- The samples were subjected to thermal cycling in accordance with IEC60068-2-82. The temperature range was -55ºC to +85ºC, with 10-minute dwells for a total of 9 days.

- Microanalysis was performed using scanning electron microscopy (SEM) after the thermal cycling was completed.
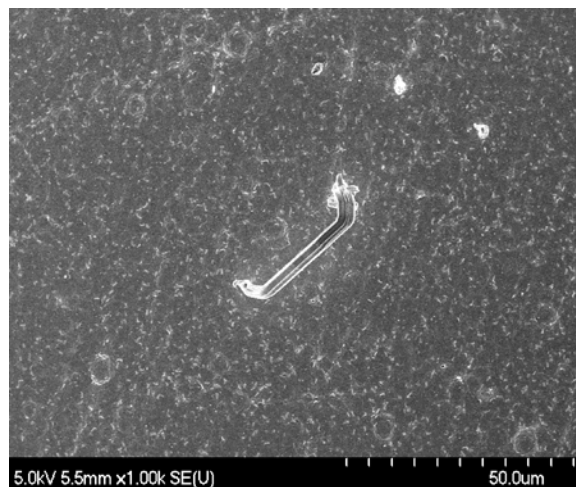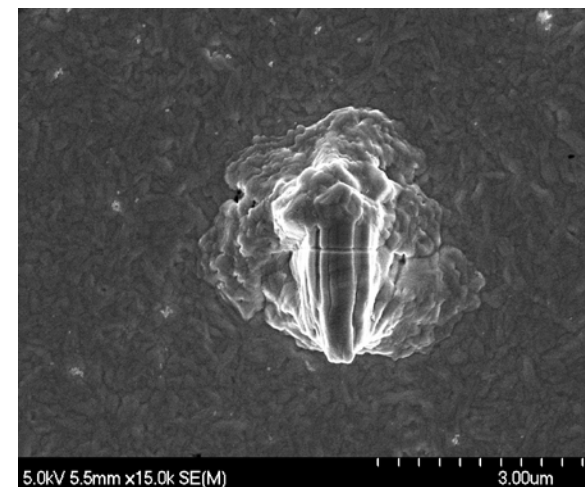
Tin Whiskering

- Of the **14** bright tin samples prepared using a 'nanocopper' underlayer, only **3** showed evidence of whiskering.
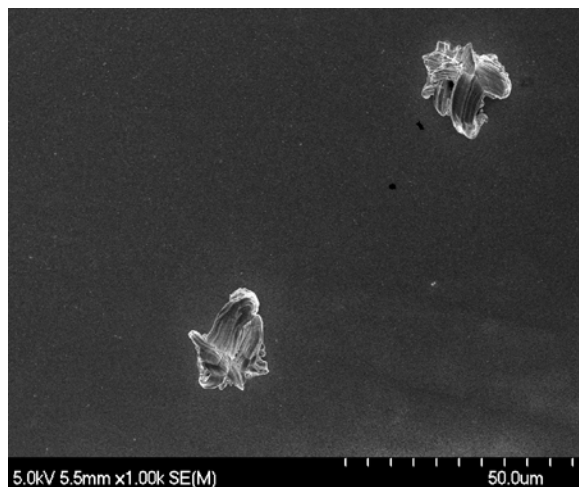
Bright Nanocrystalline Tin
(pulsed 0.1ms:0.9ms, grain refiner 50g/L)

Bright Nanocrystalline Tin
(pulsed 1ms:9ms, grain refiner 50g/L)

Bright Nanocrystalline Tin
(pulsed 0.1ms:0.9ms, grain refiner 100g/L)

Tin Whiskering

- Matte tin on *Poly*crystalline Copper **did** form whiskers.
- Matte tin on *Nano*crystalline Copper **did not** form whiskers.
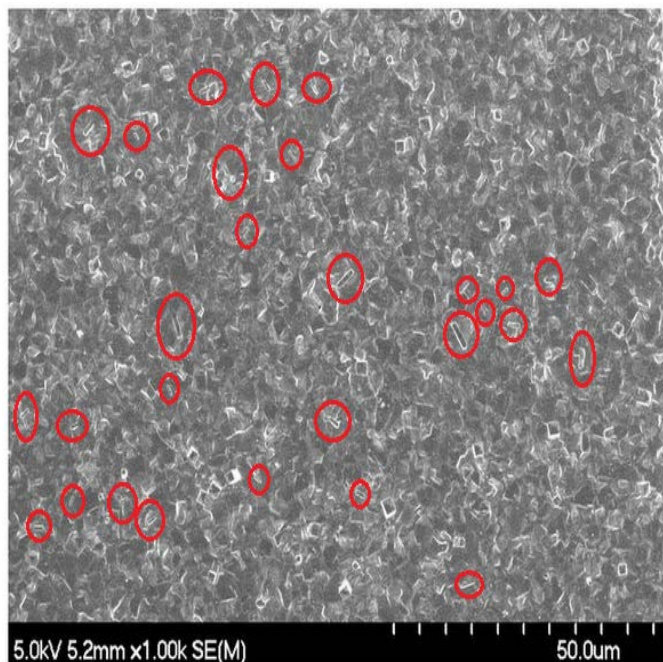
5.0kV 5.2mm ×1.00k SE(M)   50.0um

Matte Polycrystalline Tin
on Polycrystalline Copper
(Control Sample)

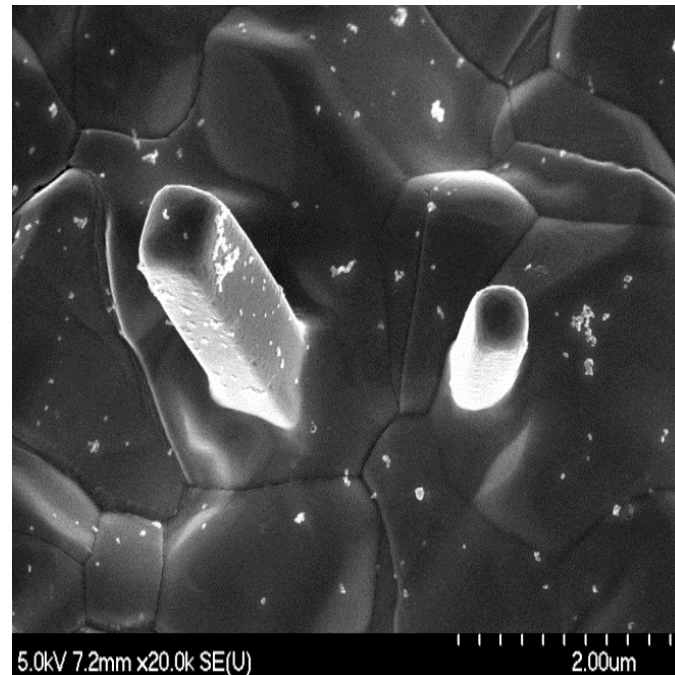5.0kV 5.5mm ×1.00k SE(M)   50.0um
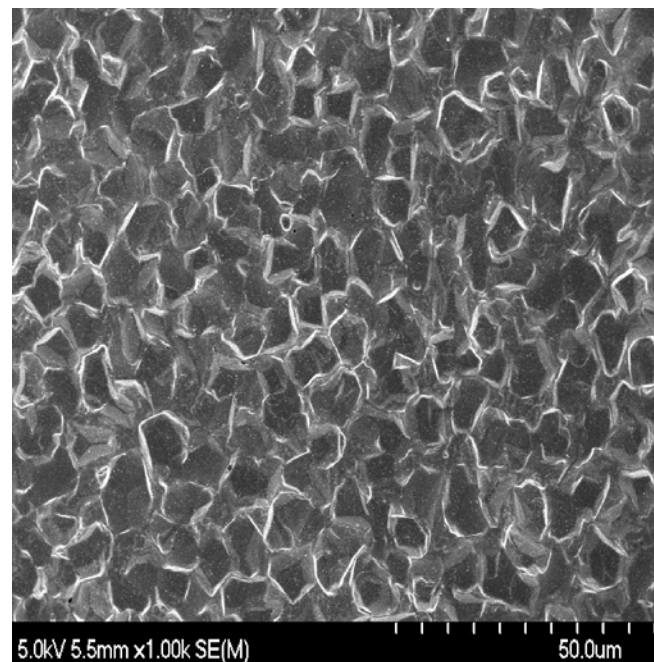
Matte Polycrystalline Tin
on Nanocrystalline Copper
(Control Sample)

Tin Whiskering

- A variety of whisker morphologies were observed, including the classical striated needle-like filaments, odd-shaped eruptions, hillocks, and smooth, rectangular-shaped growths
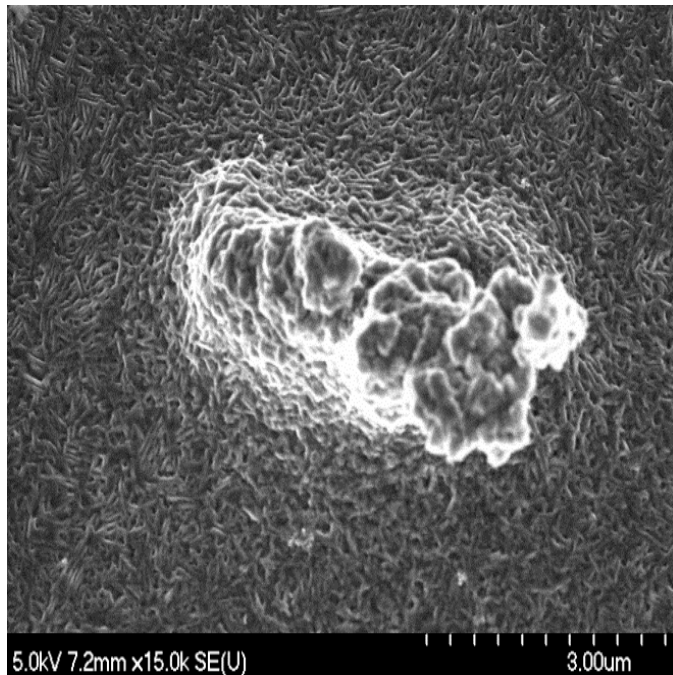
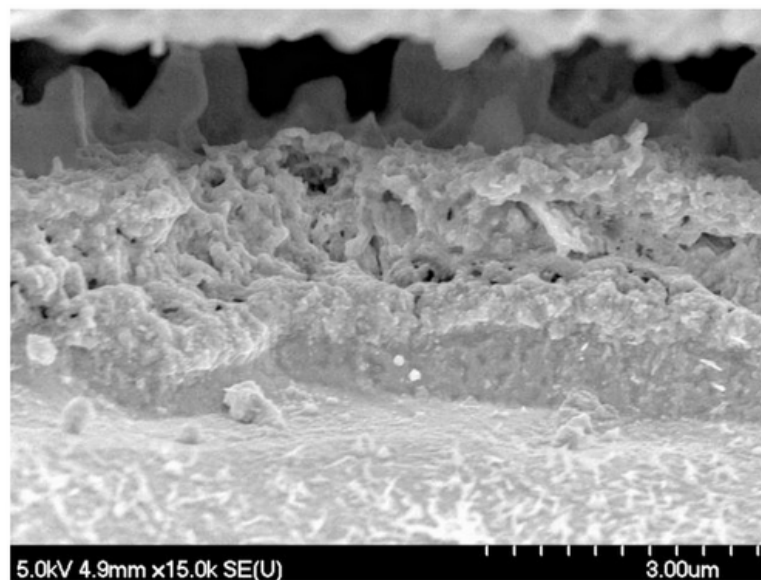Hillock in Bright Polycrystalline Tin on Nanocrystalline Copper

Smooth, "Rectangular" Whiskers in Matte Polycrystalline Tin on Polycrystalline Copper

Intermetallic Compounds
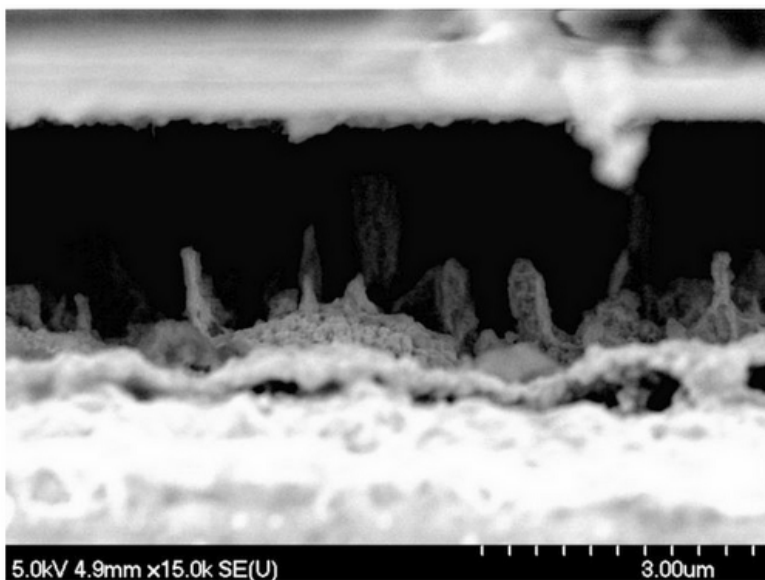
Bright Polycrystalline Tin on Nanocrystalline
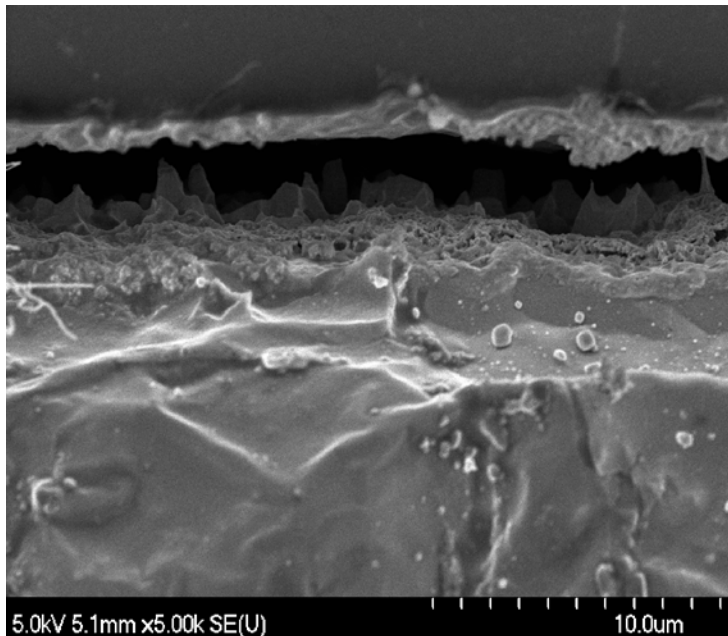Copper
(Control Sample)

Bright Nanocrystalline Tin on
Nanocrystalline Copper
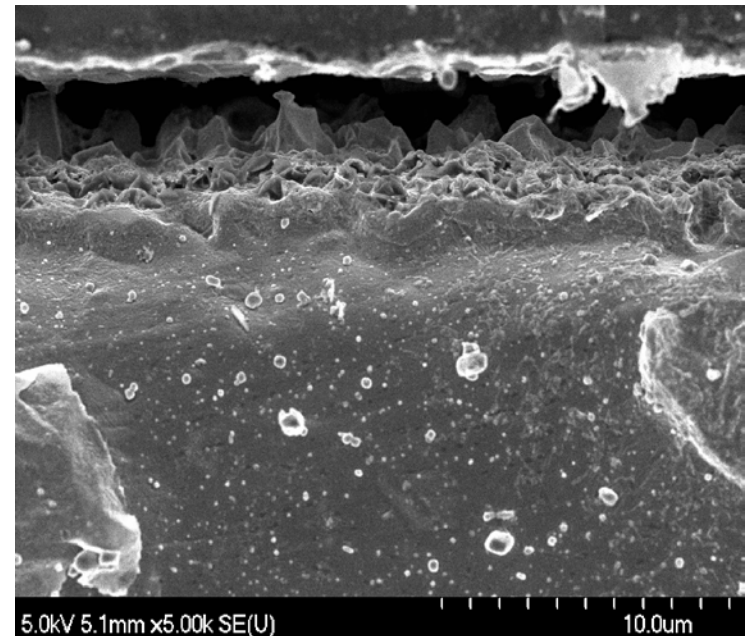(pulsed 1ms: 50ms, grain refiner 100g/L)

Intermetallic Compounds

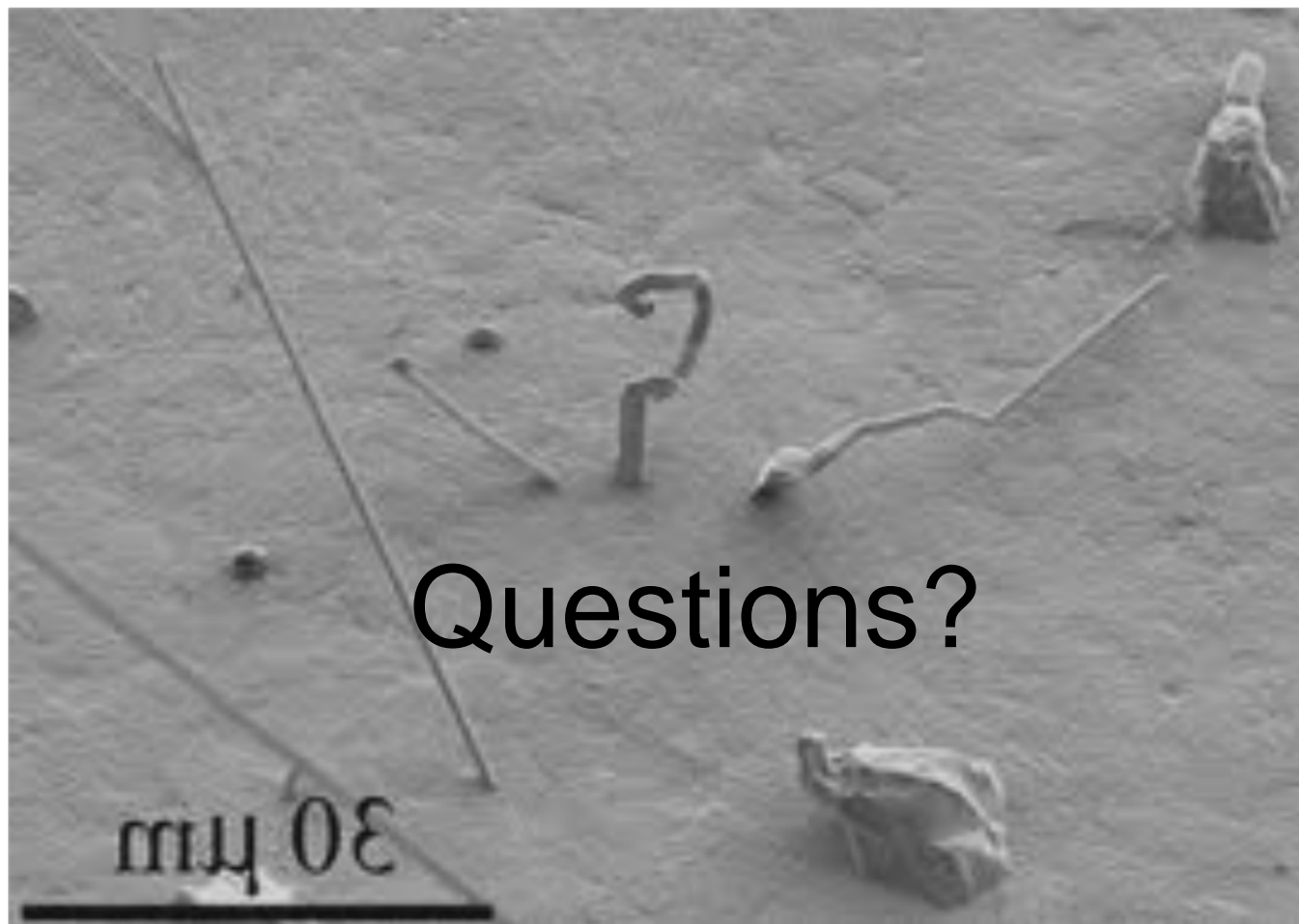Matte Polycrystalline Tin on Nanocrystalline Copper
(Control Sample)

Matte Nanocrystalline Tin on Nanocrystalline
Copper(pulsed 1ms: 50ms, grain refiner 100g/L)

Conclusions

- We have successfully demonstrated the ability to modify the grain size, shape, and texture of tin through pulse plate deposition and the addition of a grain refining additive.

- Preliminary imaging suggests that nanocopper underlayers prevent/delay whiskers from forming in polycrystalline tin, while polycrystalline copper underlayers do not – an inversion of our previous finding[1].

- There may be an increase in intermetallic compound volume in samples with grain refined tin on nanocrystalline copper.

- Our intent is to conduct ambient aging of all 28 samples over the coming year, and to perform follow-on microscopy analysis to evaluate any differences in whiskering propensity with respect to the degree of nanotexturization and/or surface smoothing.

Questions?

Image source: www.nist.gov