Effects of Tin Whisker Formation on Nanocrystalline Copper

David M. Lee, Lesly A. Piñol

Johns Hopkins Applied Physics Laboratory Laurel, MD

Spontaneously forming tin whiskers, which emerge unpredictably from pure tin surfaces, have regained prevalence as a topic within the electronics research community. This has resulted from the ROHS-driven conversion to "lead-free" solderable finish processes. Intrinsic stresses (and/or gradients) in plated films are considered to be a primary driving force behind the growth of tin whiskers. This paper compares the formation of tin whiskers on nanocrystalline and conventional polycrystalline copper deposits. Nanocrystalline copper under-metal deposits were investigated, in terms of their ability to mitigate whisker formation, because of their fine grain size and reduced film stress. Pure tin films were deposited using matte and bright electroplating, electroless plating, and electron beam evaporation. The samples were then subjected to thermal cycling conditions in order to expedite whisker growth. The resultant surface morphologies and whisker formations were evaluated.

Introduction

The past few years (since the EU's RoHS directive took effect in 2006) have seen a rapid and near-total conversion to lead-free solder technology, industry wide. Some industry players continue to enjoy 'exemptions' from the directive (i.e., military, space, and biomedical agencies), but they are facing increased pressure to conform to RoHS guidelines, since component availability is leaving them little alternative. Some resort to mixed assembly (i.e., lead-free solder balls attached using traditional tin-lead solder paste), especially for applications constrained by temperature resistance. Regardless of the method of component attachment, almost all electronics today contain some form of lead-free solder/finish, comprised of either pure tin or of tin alloys such as tin-silver-copper (SAC) solder. Given this widespread removal of lead from electronic systems, there is correspondingly a widespread potential risk of failure due to tin whiskers.

Tin whiskers are micro-scale metal filaments that can emerge unpredictably from pure tin surfaces. They are conductive and can be quite long (>2.0mm) under certain circumstances, thus creating the potential for electrical shorts between closely spaced wires and joints. Known in the literature since at least 1946 [1], the exact cause of tin whiskers is still not fully understood. The discovery that small amounts of lead could fully mitigate tin whisker growth led to 60 years of mainstream use of tin-lead eutectic solder. Scientific publications seeking to elucidate tin whisker causal effects have had very mixed results. Identically prepared samples under the same testing conditions would yield different results. For example, some samples would whisker and some would not; some would grow whiskers rapidly (days), others would take months; and some would produce nodule-like 'hillocks' while others would produce needle-like filaments.

Many theories have been advanced for the mechanisms behind whisker growth **[2]**, but an experimental counter example can always be found. None of the theories have provided the definitive answer. It is, however, widely believed that the morphology of tin films and their underlying substrates play a role in whisker development, along with stress and environmental conditions. This work explores the differences in tin whiskering propensities of pure tin surfaces with respect to the underlying copper grain structure and the type of tin deposition method used.

Background

It has been demonstrated that nanocrystalline copper deposits produced by pulsed electro deposition (PED) have a higher hardness, lower friction coefficient, and lower electrical resistance when compared to polycrystalline deposits produced by direct current (DC) plating [3].

The deposition of nanostructure deposits is possible by employing PED rectification and 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.

The objective of this study is to determine if the improved electrochemical, mechanical and physical properties and the fine grain structure of nanocrystalline copper deposits are superior to polycrystalline copper deposits in mitigating tin whisker growth.

Test substrates were plated with nanocrystalline and polycrystalline copper deposits. The mechanical and morphological properties of copper deposits were evaluated. Pure tin was then deposited on the coupons using electron beam evaporation, electroless plating, matte and bright electroplating. The samples were subjected to thermal cycling and evaluated for tin whisker growth.

Experimental Detail

The test substrates used in this study were 1”x1”x 0.010” copper substrates. Nanocrystalline copper deposits were produced by PED rectification in a copper plating bath consisting of copper sulfate, ammonium sulfate and citric acid as a grain refining additive. The deposits were plated to a thickness of 5 microns using a current density of 0.165A/in^2 at a peak current of 10A. Nanocrystalline deposits with various grain sizes were obtained by adjusting the pulse length (time on) and the time between two pulses (time off). Test substrates were plated with polycrystalline copper deposits from a standard copper sulfate process using DC rectification.

One micron of pure tin was then deposited on each sample type using, electron beam evaporation, electroless plating, matte and bright electroplating.

We selected a thickness of one micron, since it is below 20 µm, the upper whisker-mitigating threshold suggested by Ostermann [4], but also because it is the lower-threshold, below which whisker growth is also retarded. The matte and bright tin deposits were electroplated at a current density of 0.083A/in^2 with pure tin anodes at 25°C using mechanical agitation. The electroless tin was deposited at 55°C using mechanical agitation with a deposition rate of 0.2 microns/min. The electron beam evaporation tin was deposited at a chamber pressure of 1.2x10^{-5} at a rate of 4.4Å/sec. at 32% power.

Copper Deposit Analysis

Scanning Electron Microscopy (SEM) was used to determine the copper deposit morphology. Table 1 shows the average grain sizes ranging from 50 to 500 nm obtained from the various pulsed duty cycles. The deposits from the polycrystalline substrate have an average grain size of about 2 microns. (Figures 1 -4)

Table 1-Average Grain Size

Substrate	Time on m/s	Time off m/s	Grain size (nm)
Nano-A	1	99	50
Nano-B	1	50	100
Nano-C	8	99	500
Poly-D	DC	DC	2000

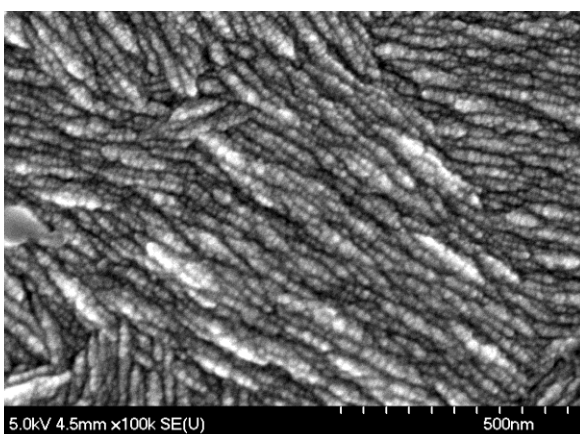

Figure 1- Substrate A 50 nm

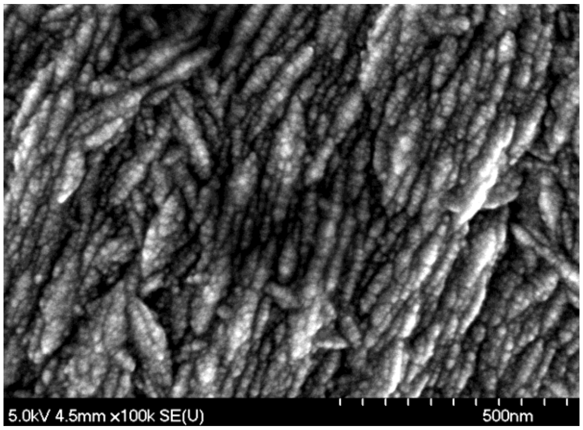

Figure 2- Substrate B 100 nm

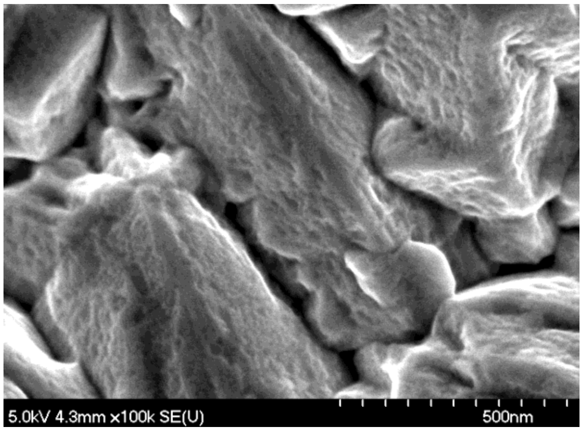

Figure 3- Substrate C 500 nm

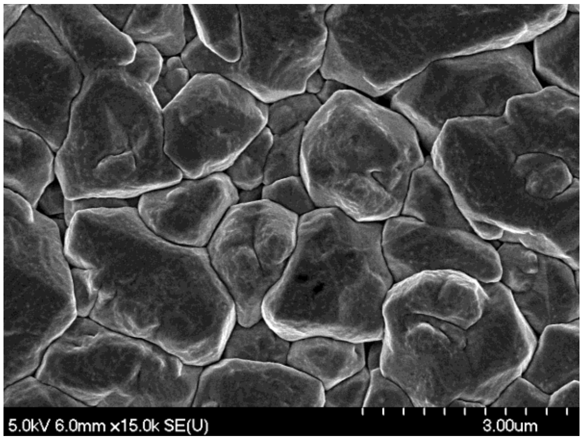

Figure 4- Substrate D 2000 nm

Hardness Test
Hardness tests were performed with a Clark MHT-1 microhardness tester using a Vickers diamond pyramidal indenter, with an applied force of 50g for 10 seconds. A low force was selected, in order to isolate measurement to the plating layer only. The hardness measurements in Table 2 show as the grain size is reduced the deposit becomes harder.

Table 2- Hardness Test

Substrate	Grain size (nm)	Force (g)	Hardness (GPa)
Nano-A	50	50	1.62
Nano-B	100	50	1.54
Nano-C	500	50	1.09
Poly-D	2000	50	0.42

Surface Roughness

The surface roughness was measured with a DEKTAK 6M Stylus Profilometer. A 1000 micron linear scan was taken within each of the four corners as well as from the center, on one representative substrate from each plating condition. The results in Table 3 show that the surface roughness of the nanocrystalline deposits is considerably less than the polycrystalline deposits.

Table 3 -Surface Roughness Measurements

Substrate	Surface Roughness (RA)
Nano-A	198
Nano-B	206
Nano-C	257
Poly-D	892

Copper Deposit Stress

The stress in the copper deposits was measured with a KLA Tencor FLX Film Stress Measurement System. Sample substrates comprised of 3 inch silicon wafers which had been metalized with 5 microns of copper using electron beam evaporation, followed by 5 microns of electroplated copper using one of four plating conditions, referenced herein as Nano-A, Nano-B, Nano-C, and Poly-D. The stress was first measured after the evaporation step (for background), and then again after electroplating. The data in Table 4 shows a moderately high initial tensile stress in the evaporated thin film. The electroplated film stress is lower due to the increased thickness of the plating. The nanocrystalline deposits have a higher tensile stress then the polycrystalline copper deposits.

Table 4- Copper Deposit Stress Measurements

Substrate	E-Beam Deposit (MPa)	Electroplated Deposit (MPa)
Nano-A	89	48
Nano-B	87	46
Nano-C	87	57
Poly-D	87	26

Table 5 - Whiskering Statistics

	After 60 Thermal Cycles (-55C to 85C, 10 min dwell)		After 124 Thermal Cycles (-55C to 85C, 10 min dwell)	
	Typical Whisker Length (μm)	Whisker Density (500X)	Typical Whisker Length (μm)	Whisker Density (500X)
Electron Beam Evaporation				
Poly D	2	163	5	323
Nano A	5	40	5	40
Nano B	3	35	3	40
Nano C	3	40	3	40
Bright Electroplating				
Poly D	0.1	190	0.1	190
Nano A	6	36	6	52
Nano B	0	0	0	0
Nano C	5	72	5	46
Matte Electroplating				
Poly D	0	0	0	0
Nano A	0.25	3800	0.5	3500
Nano B	5	162	5	350
Nano C	10	186	10	3750
Electroless Plating				
Poly D	0	0	0	0
Nano A	0	0	0	0
Nano B	0	0	0	0
Nano C	0	0	0	0

Thermal Cycling

After tin deposition (whether by plating or by physical vapor deposition), the samples were subjected to thermal cycling in accordance with IEC60068-2-82. The temperature range was -55°C to +85°C, with 10min dwells, for a total of 124 cycles. Microanalysis was performed using scanning electron microscopy (SEM) after 60 cycles had completed, and again once all 124 cycles were completed. Whisker statistics (average length and density per unit area) were compiled and are presented in Table 5. Electron beam evaporated and matte electroplated films showed further whisker growth/evolution between 60 and 124 cycles, while bright electroplated and electroless plated films did not.

Analysis and Discussion

A collection of plan-view SEM micrographs was completed (see Figure 5). Sample analysis was based on the statistics gathered after all 124 thermal cycles were completed. In the case of electron-beam evaporated films, we found a significantly reduced incidence of whiskering, with similar mean whisker lengths, for all three formulations of nanocrystalline copper underlayer (Nano A, B, and C). In the case of bright electroplated films, we found a significantly reduced incidence of whiskering, but with much longer mean whisker lengths, for the Nano A and Nano C underlayers. Bright electroplated films with a Nano B underlayer did not whisker at all. Matte electroplated films were whisker-free when a polycrystalline copper underlayer was employed however Nano B caused moderate whiskering, and Nano A and Nano C caused extremely high levels of whiskering. Electroless films were whisker-free for all sample sets.

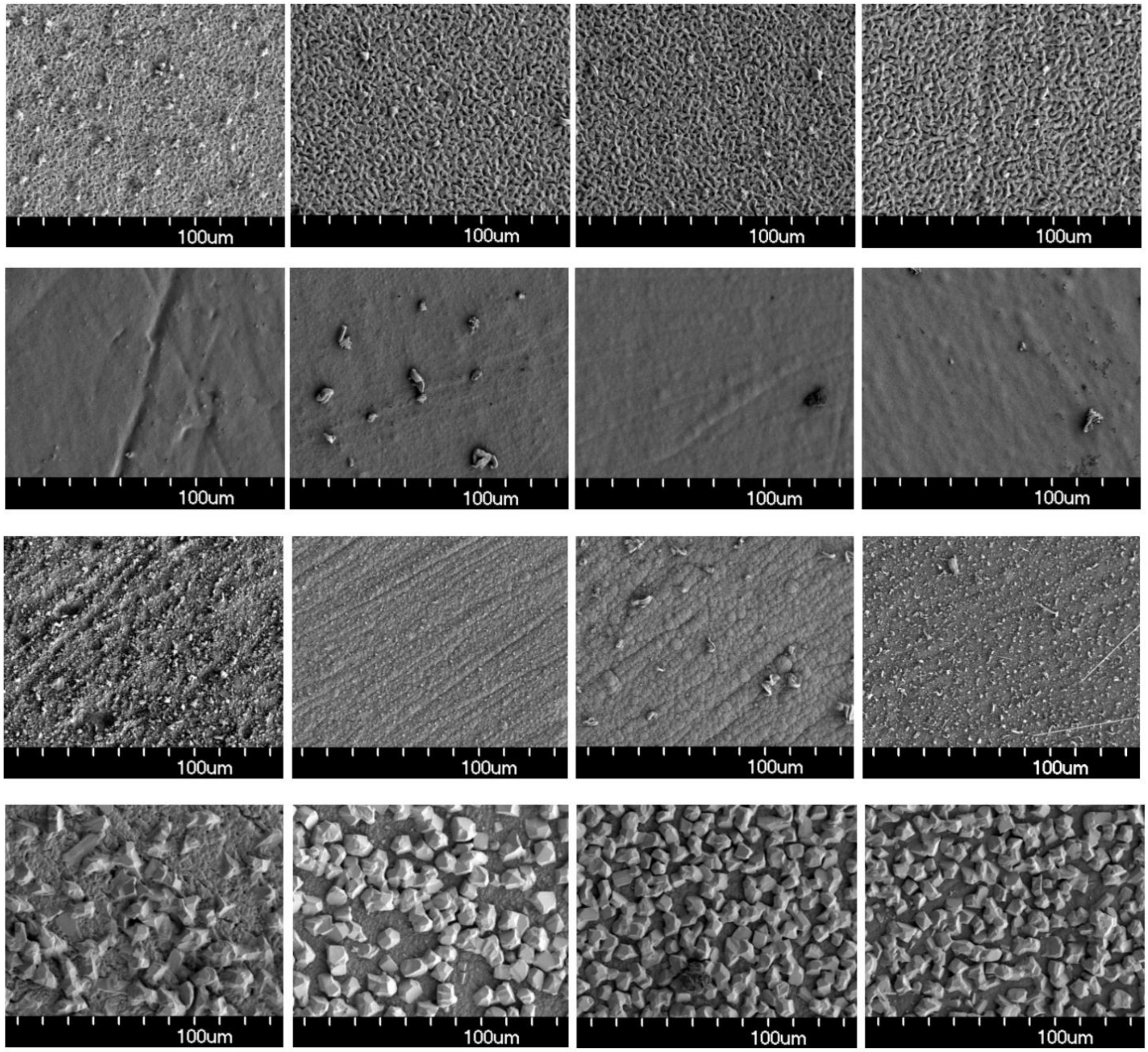

Figure 5 – Compilation of SEM Micrographs. Rows, from the top down, correspond to evaporated, bright electroplated, matte electroplated, and electroless plated films, respectively. Columns, from left to right, correspond to the type of copper underlayer (polycrystalline, Nano A, Nano B, and Nano C, respectively). Figures 6-8 shows examples of whiskering.

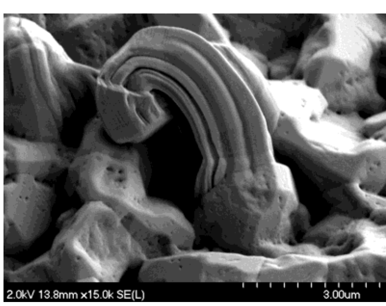

Figure 6- Nano A Evaporated

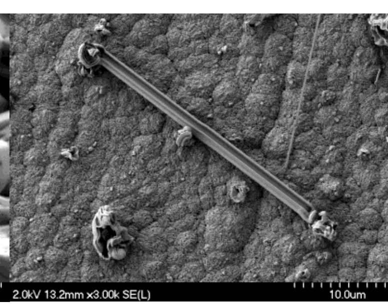

Figure 7 -Nano B Matte EP

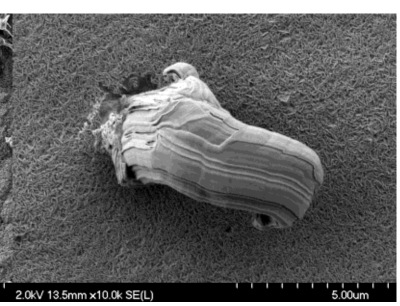

Figure 8 -Nano C Bright EP

It is theorized that samples with a higher tin surface area, such as the matte tin on polycrystalline copper, or any that were electrolessly plated, are better able to relieve stresses in-plane, reducing the need for out- of-plane whisker growth. As such, evaporated and bright tin films demonstrated moderate levels of whiskering, and matte films whose surface finish is smoothed by the presence of nanocrystalline copper underlayers whisker profusely. In cases where nanocopper reduced the amount of whiskering, we also propose that some stress compensation is taking place, given the higher tensile stress in nanocopper when compared with polycrystalline copper, to offset the compressive stress intrinsic to the tin layer. Although organic contamination is often blamed [**5, 6**] as being a likely cause of intrinsic stresses in plated films, we found no empirical evidence of this. In fact, evaporated films, deposited under high-vacuum (ostensibly clean) conditions, produced whiskers just as readily as the bright ones, and in some cases those whiskers were considerably longer.

Conclusions

Nanocrystalline copper as a whisker mitigating underlayer for pure tin finishes had mixed results after exposure to thermal cycling. The whisker density was reduced when tin was deposited by evaporation or bright electroplating. Whiskers were eliminated entirely when electroplated with bright tin on deposits with an average grain size of 100nm (Nano B) . Matte electroplated films did not whisker on polycrystalline copper, but whiskered moderately on Nano B and profusely on deposits with an average grain size of 50nm (Nano A) and 200nm (Nano C). Electroless plated films were not found to whisker under any circumstance. This may be a result of the very porous deposit of the electroless tin at a thickness of 1 micron. The lack of stress in the porous deposit may have reduced the potential for whiskering.

Lead-free solder is a reality in today's microelectronics industry, and poses many challenges, the principal of which is the ubiquitous nature of tine whiskers. Since lead-free solder has the potential to perform well for ultra fine-pitch substrates, given its superior wettability and decreased susceptibility to "bridging" over eutectic tin-lead solder, it is critically important that a robust whisker mitigation strategy be developed.

References

[1] K.G. Compton, A. Mendizza, and S.M. Arnold, "Filamentary Growths on Metal Surfaces - Whiskers," *Corrosion*, 7 (10) pp. 327-334, Oct. 1951.

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

[3] Song Tao1 and D Y Li Tribological, mechanical and electrochemical properties of nanocrystalline copper deposits produced by pulse electro-deposition (2006) Nanotechnology 17 (2006) 65–78 Institute Of Physics Publishing

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

[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.

[6] M. Dittes, P. Oberndorff, L. Petit, "Tin Whisker Formation Results, Test Methods, and Countermeasures," *Proceedings of the IEEE Electrical Components Conference*, pp. 822-826, May 2003.

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Johns Hopkins Applied Physics Laboratory Laurel, MD

JOHNS HOPKINS
UNIVERSITY
Applied Physics Laboratory

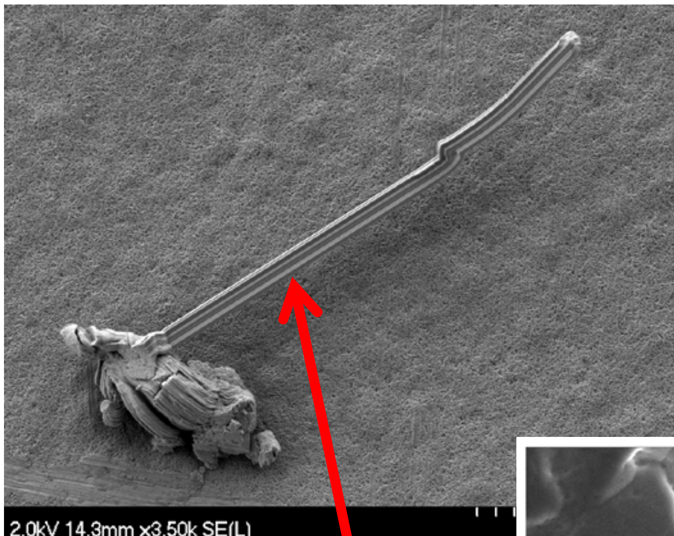
RoHS Directive

- Widespread conversion to lead-free solder technology
- Potential risk for failure due to tin whiskers
- Exemptions for military, space, and biomedical agencies, but SnPb parts are less available

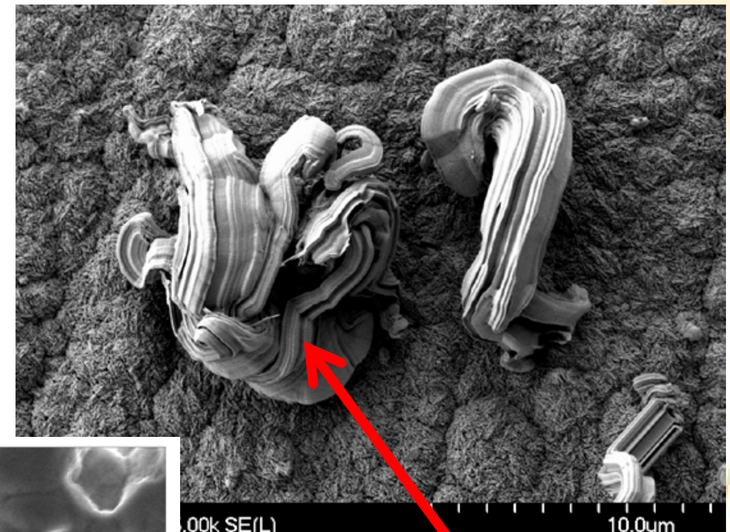
Tin Whiskers

- Micro-scale metal filaments that can emerge unpredictably from pure tin surfaces
- Conductive and can be greater then 2.0mm long
- Shorting hazard (point-to-point, debris)
- Some whiskers grow rapidly (days), others take months and even years

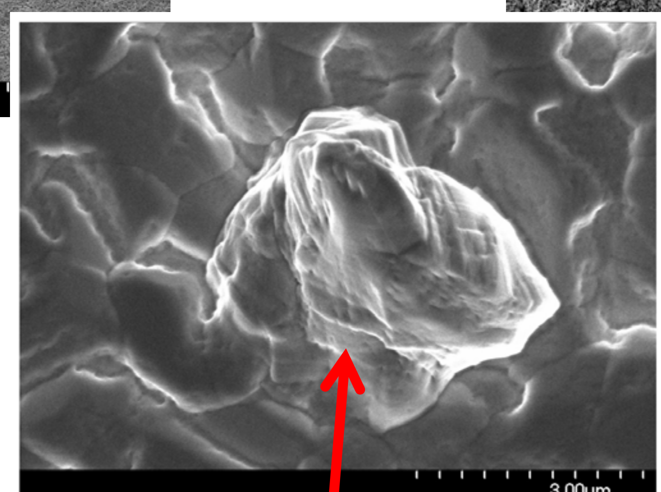
Examples of Tin Whiskers



Needle-like filaments



‘Odd Shaped Eruptions’ (OSEs)



Hillocks

Whisker Formation Theories

Possible Mechanisms

- A compressive stress state
- A stress gradient
- Metallurgical recovery (creep, recrystallization)

Possible Factors

- Organic contamination
- Cu_6Sn_5 intermetallic
- Environmental/storage conditions
- Film morphology (grain size/type, dislocations)
- Substrate properties

Types of Copper

Polycrystalline

- Typical direct current (DC) electrodeposition of conventional metals produces deposits that are polycrystalline in nature
- Polycrystalline deposits have an average grain size of **2 µm**

Nanocrystalline

- Nanocrystalline deposits produced by pulsed electrodeposition (PED) have an average grain size of **100nm**
- The addition of organic additives aids in inhibiting crystallite growth, resulting in a finer grained structure
- Higher hardness
- Lower friction coefficient
- Lower electrical resistance

Study Objectives

To determine if nanocrystalline copper deposits are superior to polycrystalline copper in mitigating tin whisker growth

To evaluate the mechanical & morphological properties of nanocrystalline and polycrystalline copper deposits

To deposit pure tin onto test substrates using electron beam evaporation, electroless plating, matte and bright electroplating

To examine the effects of thermal cycling on tin whisker growth

Experimental Detail

- Test coupons were 1”x1”x 0.010” copper substrates

- Nanocrystalline copper
  - PED rectification in a copper plating bath consisting of copper sulfate, ammonium sulfate and citric acid as a grain refining additive
  - Various grain sizes were obtained by adjusting the pulse length (time on) and the time between two pulses (time off)
  - Plated to a thickness of 5 µm
    - Current density = 0.165A/in^2
    - Peak current = 10A

- Polycrystalline copper (for reference)
  - Standard copper sulfate process using DC rectification

Nanocrystalline Copper Deposit Average Grain Size

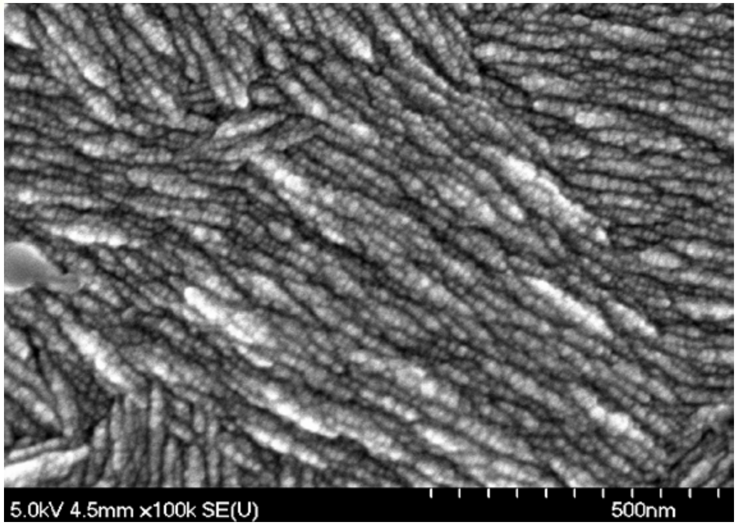
Substrate	Time on m/s	Time off m/s	Grain size (nm)
Nano-A	1	99	50
Nano-B	1	50	100
Nano-C	8	99	500
Poly-D	DC	DC	2000

Tin Deposition

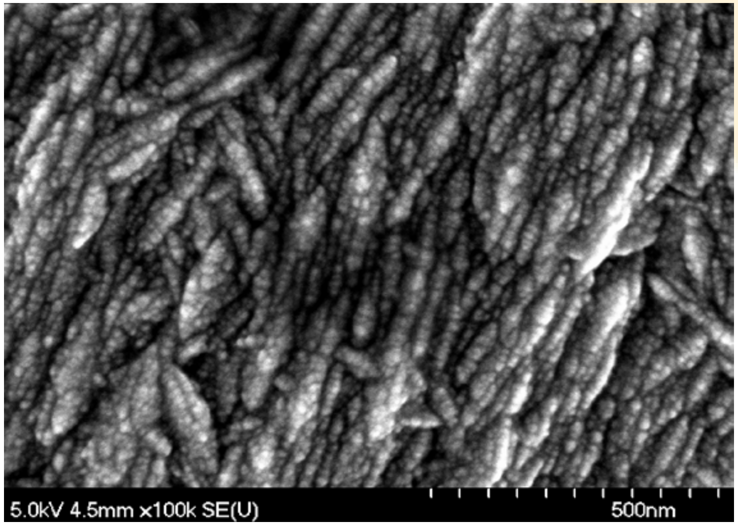
One micron of pure tin was deposited onto each sample type.
A thickness of 1µm is not considered to be whisker-mitigating.

Electron beam evaporation	• Base pressure = $1.2x10^{-5}$ Torr • Rate = 4.4Å/second at 32% power
Matte electroplating	• Current density = $0.083 A/in^2$ • Pure tin anodes at 25° C using mechanical agitation
Bright electroplating	• Current density = $0.083 A/in^2$ • Pure tin anodes at 25° C using mechanical agitation
Electroless plating	• Deposited at 55° C using mechanical agitation • Rate = 0.2 microns/min

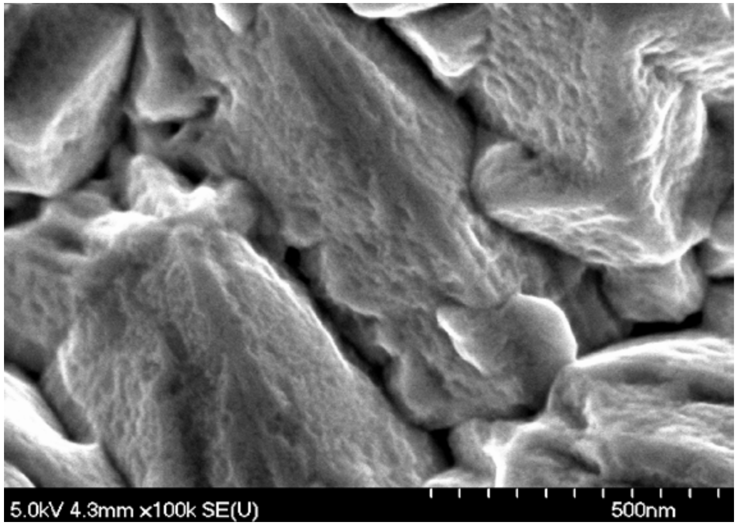
Copper Deposit Analysis



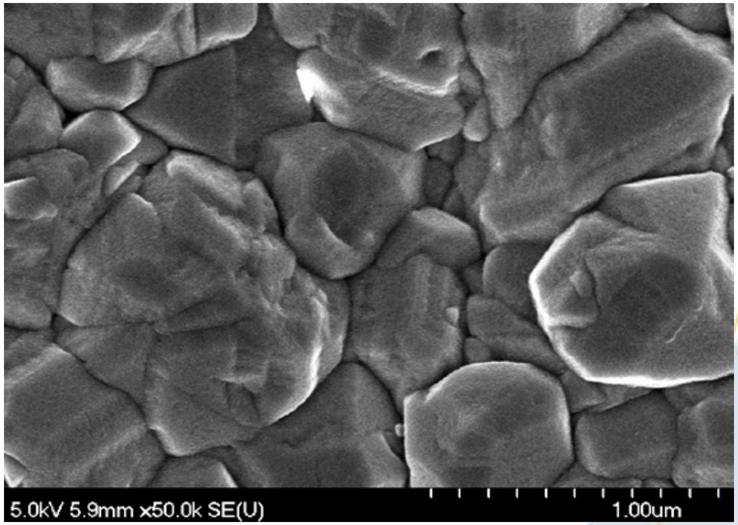
Nano A 50 nm



Nano B 150 nm



Nano C 500 nm



Poly D 2000 nm

Hardness Test

- A Clark MHT-1 microhardness tester with a Vickers diamond pyramidal indenter was used, with an applied force of 50g for 10 seconds.

- A low force was selected in order to isolate measurement to the plating layer only.

- The hardness values show that as grain size is reduced the deposit becomes harder.

Substrate	Grain size (nm)	Force (g)	Hardness (GPa)
Nano-A	50	50	1.62
Nano-B	100	50	1.54
Nano-C	500	50	1.09
Poly-D	2000	50	0.42

Surface Roughness

- Surface roughness was measured with a DEKTAK 6M Stylus Profilometer.

- 1000 µm linear scans were taken at 5 locations (all four corners and center) on one representative substrate from each plating condition.

- Results show that the surface roughness of the nanocrystalline deposits is considerably less than the polycrystalline deposits.

Substrate	Surface Roughness (RA)
Nano-A	198
Nano-B	206
Nano-C	257
Poly-D	892

Copper Deposit Stress Analysis

• The stress in the copper deposits was measured with a KLA Tencor FLX Film Stress Measurement System.

Sample Description:

3” silicon wafers which had been metallized with 5 µm of copper using electron beam evaporation, followed by 5 microns of electroplated copper using one of four plating conditions

Findings:

The data shows a moderately high initial tensile stress in the evaporated thin film.

The electroplated film stress is lower due to the increased thickness of the plating

The nanocrystalline deposits have a higher tensile stress then the polycrystalline copper deposits

Substrate	E-Beam Deposit (MPa)	Electroplated Deposit (MPa)
Nano-A	89	48
Nano-B	87	46
Nano-C	87	57
Poly-D	87	26

Thermal Cycling

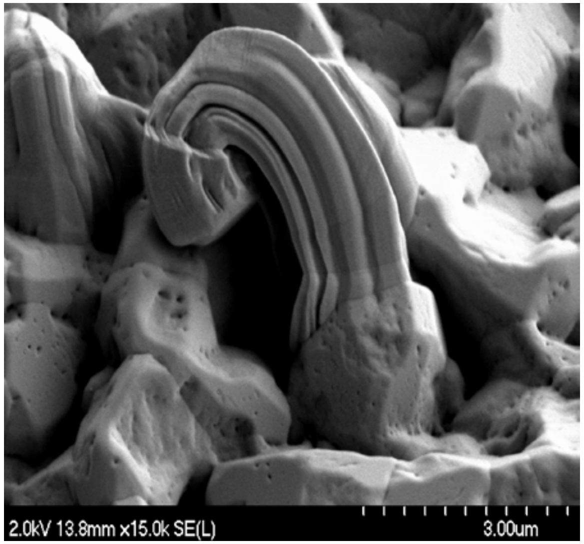
- Performed in accordance with IEC60068-2-82
  - The temperature range was -55° C to +85° C
  - 10 minute dwells
  - 124 cycles total

- Scanning electron microscopy (SEM) analysis was performed after 60 and 124 cycles.

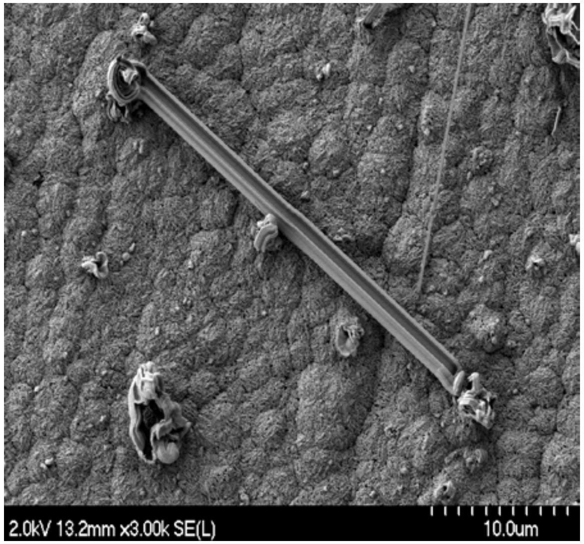
- Electron beam evaporated and matte electroplated films showed further whisker growth/evolution between 60 and 124 cycles, while bright electroplated and electroless plated films did not.

- Whisker statistics (average length and density per unit area) were compiled

Examples of Whiskering



Nano A Evaporated



Nano B Matte Electroplated

Nano C Bright Electroplated

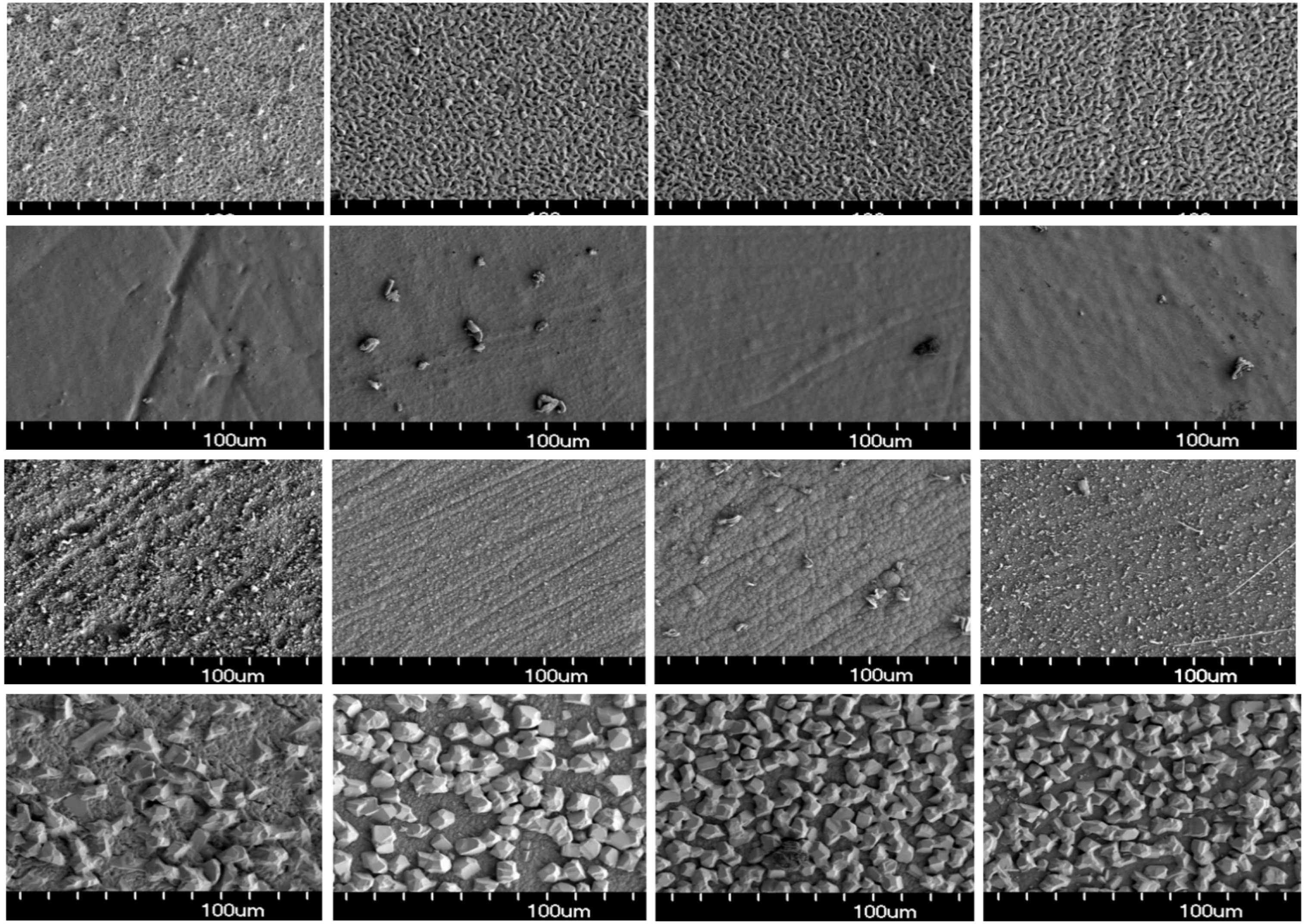
SEM Micrographs

Evaporated

Bright Electroplated

Matte Electroplated

Electroless plated



Polycrystalline | Nano A | Nano B | Nano C

Whiskering Statistics

	After 60 Thermal Cycles (-55C to 85C, 10 min dwell)		After 124 Thermal Cycles (-55C to 85C, 10 min dwell)	
	Typical Whisker Length (µm)	Whisker Density (500X)	Typical Whisker Length (µm)	Whisker Density (500X)
Electron Beam Evaporation				
Poly D	2	163	5	323
Nano A	5	40	5	40
Nano B	3	35	3	40
Nano C	3	40	3	40
Bright Electroplating				
Poly D	0.1	190	0.1	190
Nano A	6	36	6	52
Nano B	0	0	0	0
Nano C	5	72	5	46
Matte Electroplating				
Poly D	0	0	0	0
Nano A	0.25	3800	0.5	3500
Nano B	5	162	5	350
Nano C	10	186	10	3750
Electroless Plating				
Poly D	0	0	0	0
Nano A	0	0	0	0
Nano B	0	0	0	0
Nano C	0	0	0	0

Analysis and Discussion

Electron-beam evaporated films	• Significantly **reduced** incidence of whiskering for all three nano-copper underlayers (Nano A, B, and C) when compared with PolyD.
Bright electroplated films	• Significantly **reduced** incidence of whiskering for all three nano-copper underlayers (Nano A, B, and C) when compared with PolyD.
Matte electroplated films	• Significantly **increased** incidence of whiskering for all three nano-copper underlayers (Nano A, B, and C) when compared with PolyD.
Electroless films	• Whisker-free for all sample sets.

Analysis and Discussion

In-Plane Stress Relief

- We propose that samples with a higher tin surface area, such as the matte tin on polycrystalline copper, or any that were electroless plated, are better able to relieve stresses in-plane, reducing the need for out- of-plane whisker growth
- Evaporated and bright tin films demonstrated moderate levels of whiskering, and matte films whose surface finish is smoothed by the presence of nanocrystalline copper underlayers whisker profusely

Stress Compensation

- In cases where nano-copper reduced the amount of whiskering, we propose a stress compensation mechanism, in which the higher tensile stress in nanocopper (when compared with polycrystalline copper) offsets the compressive stress intrinsic to the tin layer.

Unimportance of Organic Contamination

- Evaporated films deposited under high-vacuum conditions produced whiskers just as readily as the bright ones, and in some cases those whiskers were considerably longer. As such, organic additives did not appear to impact whiskering.

Conclusions

Nanocrystalline copper as a tin whisker mitigating underlayer had mixed results after exposure to thermal cycling

- Nanocrystalline copper appears to have **reduced** whiskering:
  - When tin was deposited by evaporation
  - When tin was deposited by bright electroplating
- Nanocrystalline copper appears to have **prevented** whiskering:
  - When electroplated with bright tin on deposits with an average grain size of 100nm (Nano B)
- Nanocrystalline copper appears to have **increased** whiskering:
  - When tin was deposited by matte electroplating. Whiskering was moderate on Nano B and extensive on deposits with an average grain size of 50nm (Nano A) and 500nm (Nano C)

Conclusions (cont'd)

- Electroless plated films were not found to whisker under any circumstance. This may be a result of the very porous deposit of the electroless tin at a thickness of 1 µm (the self-limiting thickness is ~10 µm).

- The lack of stress due to it being a discontinuous film may have eliminated the driving force for whiskering.

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Johns Hopkins Applied Physics Laboratory Laurel, MD

JOHNS HOPKINS
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