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Contributions of Stress and Oxidation on the Formation of Whiskers in Pb-free Solders

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14. ABSTRACT
Understanding the environmental factors influencing formation of tin whiskers on electrodeposited lead free, tin coatings over copper (or copper containing) substrates is the topic of this study . An interim report* summarized initial observations as to the role of stress and oxide formation on whisker growth. From the initial results, two main areas were chosen to be the focus of additional research: the demonstration of effects of elastic stress state in the nucleation of whiskers and the confirmation of the effect of oxygen content in the formation of whiskers. Different levels of elastic stress were induced with the incorporation of a custom designed fixture that loaded the sample in a four-point bending configuration and were maintained in an environmental chamber under conditions deemed favorable for whisker growth. The effects of oxygen content were studied by aging substrates in gas vials of varying absolute pressure and different oxygen partial pressure.

*E. N. Hoffman, P. S. Lam and X. Li, "Interim Report: Contributions of Stress and Oxidation on the Formation of Whiskers in Pb-free Solders," WP-1754

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List of Abbreviations

a	Distance between the inner and outer loading pins in 4 point bending configuration
ASTM	American Society for Testing Materials
BSE	Backscattered Electron
E&CPT	Environmental and Chemical Process Technologies
ESTCP	Environmental Security Technology Certification Program
FIB	Focused Ion Beam
I_{film}	Moment of Inertia of the film
$I_{substrate}$	Moment of Inertia of the substrate
P	Load
RH	Relative humidity
σ_{max}	Stress at the top surface of the film
SE	Secondary Electrons
SEM	Scanning Electron Microscopy
SRNL	Savannah River National Laboratory
y_{max}	Distance from the neutral axis to the top surface of the film
WD	Working Distance
WP	Weapons Systems and Platforms

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The authors would like to acknowledge the contributions of several individuals without whom this report would not be possible. X. Li (University of Virginia) and Y. Sun produced the initial electrodeposited films on various substrates and assisted performing the analysis in the initial phase of the research while at the University of South Carolina. C. A. Handwerker and Y. Wang of Purdue University produced electrodeposited tin films on both copper and glass substrates for the bend fixture tests. K. Peterson of SRNL provided the design for the static 4 point bend fixture. H. Ajo of SRNL provided the electron micro-analysis in this report. P-S Lam provided the technical review of this report. Funding was provided through ESTCP Project WP 1754. These contributions are greatly appreciated.

Executive Summary

This report summarizes the research activities of WP-1754. The study focuses on the environmental factors influencing formation of tin whiskers on electrodeposited lead free, tin coatings over copper (or copper containing) substrates. Much of the initial results are summarized in an interim report [1]. From the initial results, two main areas were chosen to be the focus of additional research: the demonstration of effects of stress state in the nucleation of whiskers and the confirmation of the effect of oxygen content in the formation of whiskers.

The preliminary observations indicate that whisker formation is proportional to compressive stress up to the elastic limit of the film. Different levels of elastic strain were induced with the incorporation of a custom designed fixture that loaded the samples in a four-point bending configuration and were maintained in an environmental chamber under conditions deemed favorable for whisker growth. The results show that induced elastic stress slightly increased the concentration of nucleation sites of whiskers.

Initial studies also showed enhanced whisker formation in dry nitrogen atmospheres. The effects of oxygen content were studied by aging substrates in gas vials of varying absolute pressure and different oxygen partial pressure. The concentration of whiskers were measured and do not appear to be sensitive to oxygen content, as previously observed [1], but do exhibit higher concentrations under vacuum.

Introduction

Metallic whisker formation has been observed in lead free films of tin, cadmium and zinc since the 1940s [2]. Increasingly, the use of lead free solder and coatings in military applications has led to higher failure rates and lower reliability of electronic components due to short circuits and electrical arcing. As technology advances reduce the scale or size of electronic devices and environmental legislation continues to increase the life-cycle cost of lead in electronics, the instances of whisker driven failures in these devices is expected to grow. In order to produce solder alloy forms that show enhanced resistance toward whisker growth, a study was proposed to increase the understanding of the role of certain environmental factors on whisker growth in lead-free solders. These environmental factors include external stress and formation of intermetallic compounds in the tin film or at the tin/substrate interface. It is expected that this understanding will support the development of a predictive model, enabling engineers to design solder alloys for whisker growth resistance.

Background

Applied compressive stress has been shown to accelerate the growth rate of whiskers [3]. Nucleation and growth of metallic whiskers has been proposed to be caused by stress in the tin film [4]. Thermal cycles, the coefficient of thermal expansion mismatch between the substrate and the surface film and density changes due to phase transformations influence the stress state of the thin films. If extreme enough, these stresses can lead to morphology changes such as whisker formation and growth. In Figure 1, an example of a tin film on a copper substrate illustrates this phenomenon. The whisker has nucleated from the grain boundary and grown directly out of the surface without coarsening or changing direction. Sometimes a kink will form and cause the direction of growth to change. In addition to whiskers, hillocks (mound like protrusions from the surface) have been observed to form in lieu of whiskers. These are generally not considered as detrimental as whiskers.

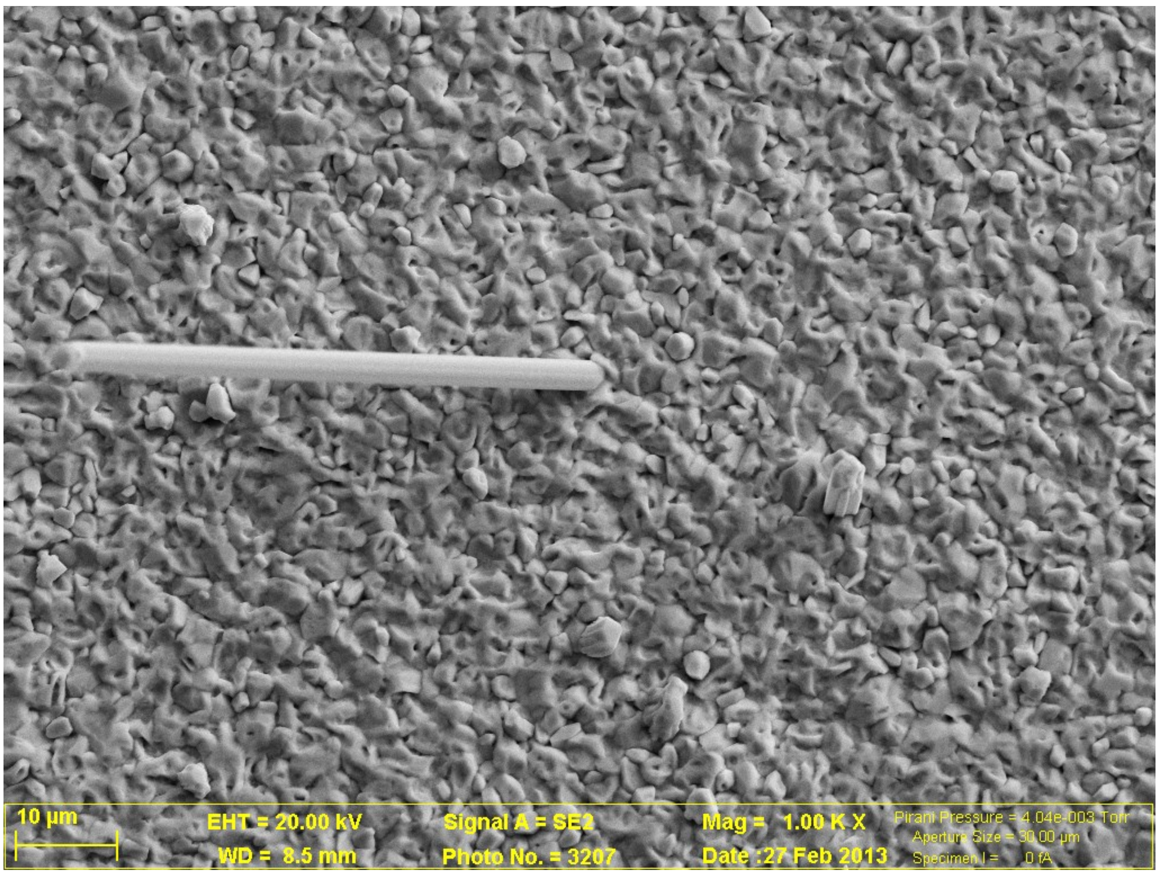


Figure 1: Secondary Electron Micrograph showing the surface of a tin film with whisker

The in-growth of stresses in thin films has been previously studied [4]. The stress state of the lead-free solder film deposited on a substrate may be obtained by measuring the curvature of the specimen then applying the classical Stoney equation published in 1909. This approach was used to model the effect of stress on nucleation sites of whiskers [1]. The model showed that some isolated areas of compressive stress in the elastic regime occurred when the substrate had external stresses applied to it. Preliminary observations showed that no whisker growth was observed on samples that were loaded beyond the yield stress of the film, but that when loads were applied in the elastic regime, whisker growth was observed on two samples [1].

Four-point bend fixtures were fabricated to provide constant load to samples and to experimentally observe if the stress state would result in accelerated whisker growth. The samples were loaded in bending, with the tin film facing toward the minor span of the loading pins, to stress levels below the yield stress of tin. Two different substrates were selected for testing: 0.6mm OFHC copper sheet and 1mm glass.

Stress does not have to be externally induced. Phase transformations play a large role in the effects of residual stresses induced in the film. The role of Cu_6Sn_5 has been shown to influence the stresses inside the thin film. As this intermetallic phase nucleates growth within the film, the magnitude of compressive stresses in the film increases but is not uniform throughout the film cross-section. The anisotropic nature of the intermetallic phases result in areas of stress concentration. In addition, radiation can cause the formation of other phases which can alter the stress state induced in the film.

Initial observation showed that samples held in 100% N_2 had enhanced whisker formation [1]. SEM analysis confirmed a difference in whisker growth between samples stored in 100% air and 100% nitrogen for 263 days. The sample stored in 100% nitrogen had an increased number of whiskers. The whiskers were also longer compared to the samples stored in 100% air. In order to verify this observation, parallel samples were held in atmospheres of 100% air and 100% N_2 to study the role of oxidation in whisker formation.

Objective

The objective of this project is to increase the understanding of the role of stress and oxide formation on whisker growth in lead-free solders. This understanding will support the future development of a predictive model, enabling engineers to design solder alloys for whisker growth resistance.

Methods

Sample Preparation: Samples for environmental testing were prepared at University of South Carolina. Samples for environmental testing were prepared by electrodeposition. Sn thin films on Cu substrates were fabricated in an electrochemical workstation (model 760D, CH Instruments, Austin, TX) with a three-electrode system. A titanium-mesh electrode with 10 µm thick platinum film was used as the counter electrode and the reference electrode was Ag/AgCl. Chemicals of analytical grade and double-distilled water were used throughout all experiments. For Sn deposition, sodium citrate tri-basic di-hydrate ($C_6H_5Na_3O_7 \cdot 2H_2O$) was added into a tin(II) chloride ($SnCl_2 \cdot 2H_2O$) aqueous solution to achieve a stable stannous solution. A potential was applied to impress a constant current density of 4 mA/cm^2 in order to deposit a homogenous and continuous thin film of metallic tin. All the samples have a spherical grain feature, which was typical for electrodeposition. The thickness of the samples was measured to be approximately 10 µm in the middle of the samples. Such thin thickness is stated to be a precondition for observable whisker growth. The cross-section image (Figure 2) also demonstrates a good bonding between the deposited films and the substrates.

Samples for static load bend testing were prepared at Purdue University by Yi Wang under the direction of C. A. Handwerker. The samples were prepared by electroplating tin films on substrates of copper and glass. For copper the substrates were dipped in 98% sulfuric acid to remove the native copper oxide and then rinsed using ultrapure water immediately before electroplating. Copper substrates were electroplated with pure tin films to a thickness of 5 µm using a commercial Sn plating solution and a pure tin anode. Electroplating was performed at a constant current density of 11 mA/cm^2 and using a cathode rotated at 200 rpm.

Tin films on glass substrates were achieved by e-beam deposition of a 10 nm Ti adhesion layer onto the glass, followed by a 300 nm Cu layer. Next, the substrates were dipped in acid as above followed by electroplating with the same conditions as the copper substrates. Microstructures of the films were characterized using SEM and FIB milling (see Figure 2).

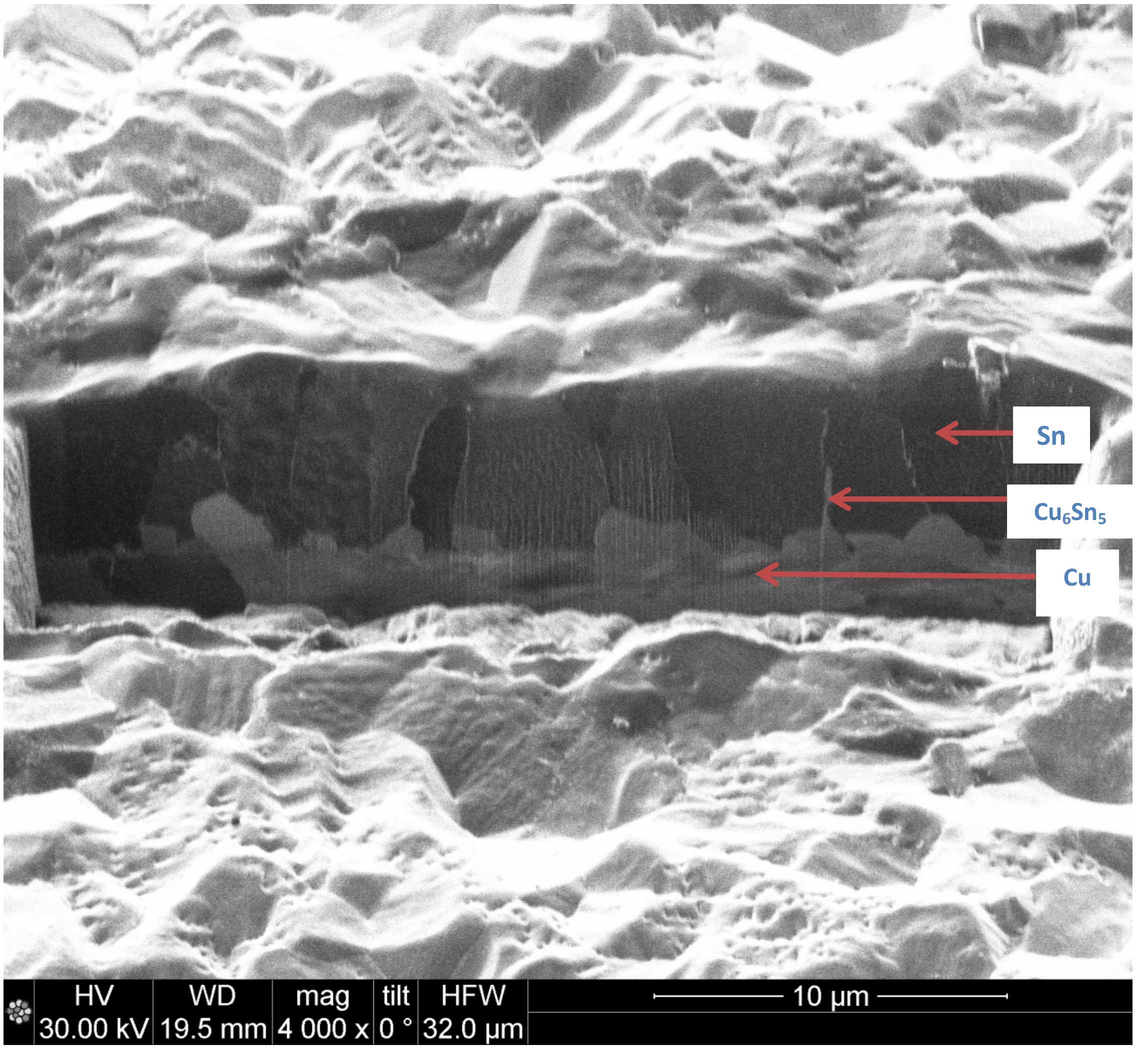


Figure 2: SEM Micrograph of Tin film on Copper Substrate cross-sectioned by FIB milling [5]

Bend Tests: Four-point bend fixtures were configured to ASTM E 855 [6] and C 1161 [7]. The bend fixtures (see Figure 3) were fabricated so samples could be statically loaded and held in an environmental chamber at constant temperature and relative humidity. The four point bend fixture had major and minor span of 24 mm and 12 mm, respectively. Two types of samples were evaluated: 1) tin films electroplated on copper substrate (35 mm length x 10 mm width x 0.6 mm thickness) and 2) tin films electrodeposited on glass with an evaporative copper coating on its surface (35 mm length x 10 mm width x 1 mm thickness). Target stresses were selected to be at or just below the yield stress of the Sn film in compression (i.e., top surface). The stress response of the substrate and film were estimated based on the bi-material strip model [8] (see Figure 4), modifying the relation for the bending configuration. The required load was determined by the relation:

$$\textbf{Moment} = \frac{\mathbf{p}}{\mathbf{2}} \times \mathbf{a} = \frac{\boldsymbol{\sigma}_{\mathbf{max}} \times \mathbf{I}}{\mathbf{y}_{\mathbf{max}}}$$

P is load
a is the distance between the inner and outer loading pins = 6 mm
$\boldsymbol{\sigma}_{\mathbf{max}}$ is the stress at the top surface of the film = 9 - 11 MPa
I: is moment of inertia of the transformed section with parallel-axis theorem
$I = I_{substrate} + I_{film} = 0.568\ mm^4$ (copper) and $1.38\ mm^4$ (glass)
$\mathbf{y}_{\mathbf{max}}$ is the distance from the neutral axis to the top surface of the film = 0.304 mm (tin on copper) and 0.503 mm (tin on glass).

The first samples (tin on copper) were loaded in the 4-point bend fixtures at SRNL. The intent was to induce compressive stresses in the tin films to determine the effect of stress level on whisker formation. The stress was held constant in conditions favorable to whisker formation (i.e., 25 °C, 10% RH). The first samples were held for approximately 32 days and unloaded to characterize the amount of whisker formation (see Figure 5). Discussions with the laboratory at Purdue led to the second type of samples consisting of tin films on top of an evaporative coating of copper on glass substrates. These samples were held for approximately 25 days (see Figure 6) and examined for whisker growth.

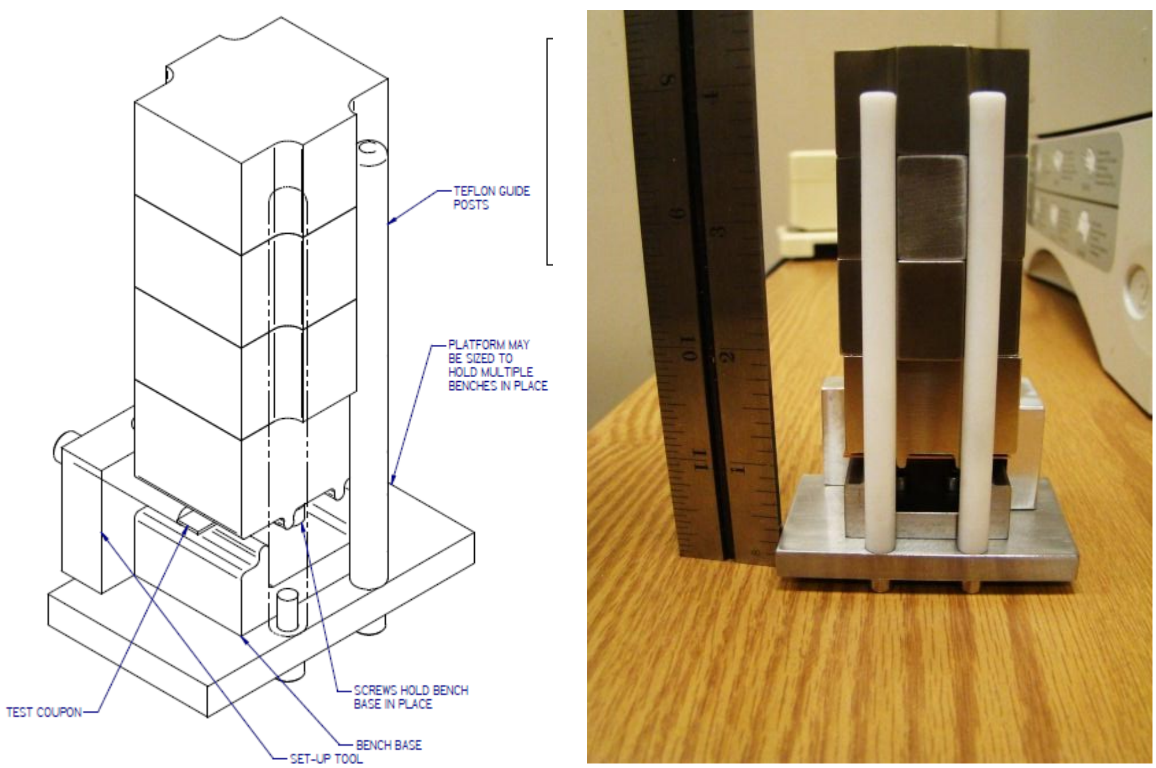


Figure 3: Four-point Bend Fixture Schematic a) and Assembled Configurations b)

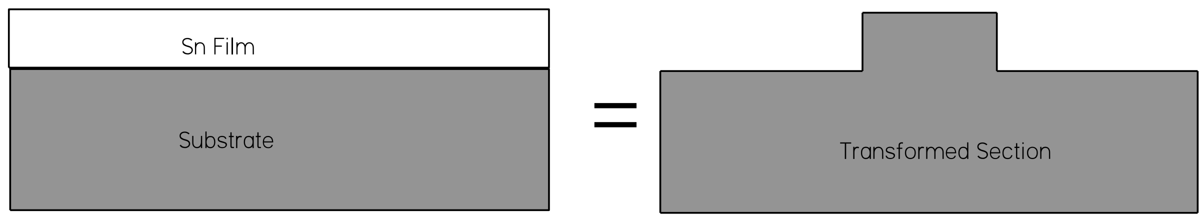


Figure 4: Transformed Section of bend specimen for bi-material strip model (not to scale)

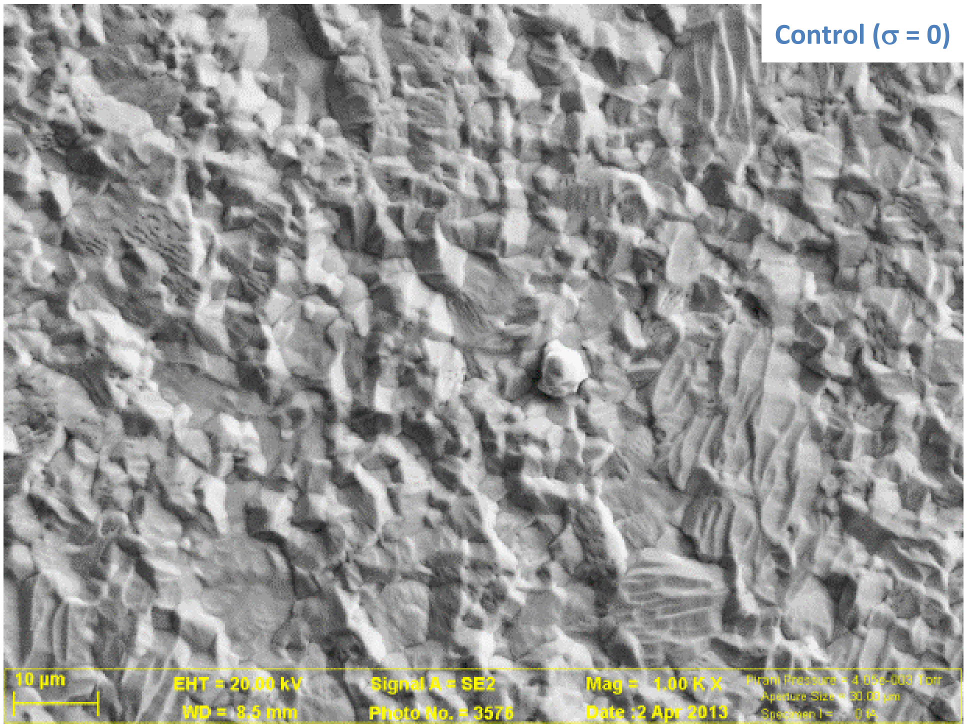
Environmental Tests: Parallel samples of 100% air and 100% N_2 atmosphere were used to study the role of oxidation in whisker formation. Tin films on copper substrates were loaded into vessels that were helium leak tested to ensure leak rates were below 1×10^{-7} std. cc He/sec. Vessels were evacuated and backfilled with gas (nitrogen or air) to absolute pressures of 0, 0.5, 1 and 4 atm (see Figure 7). The vessels were held for a period of 200 days. Immediately after opening, samples were evaluated using the SEM for whisker growth. All samples were run in duplicate. However, some vessels had leaked down to atmospheric pressure over time and thus the data were discarded.

Characterization: Substrates were examined using scanning electron microscopy under secondary electron (SE) and backscattered electron modes (BSE) immediately after the completion of their aging time. The accelerating voltage of the electron beam was 20 kV and a working distance (WD) of 8.5 mm. A minimum of 3 images were recorded for each sample at magnifications of 100X, 500X and 1000X. The concentration of hillocks/whiskers was measured by counting the number of features in the 100X field and dividing by the area. The average and standard deviation concentration for each condition was reported.

Results

The results of the bend test study are presented in Figures 5 and 6. The samples were held at constant stress in an environmental chamber for a period of time expected to allow whisker growth to occur. In Figure 5, the samples of tin films on copper substrates are presented as a function of stress. The yield stress of tin is 11 MPa, so induced stresses of 9, 10 and 11 MPa were compared to substrates with no load. The samples were held at 25 °C and 10% relative humidity for 770 hours. The results did not show substantial whisker growth on any of the samples. Hence, the concentration of whiskers was not reported for the tin on copper substrates. In Figure 6, the results from tin films on glass substrates coated with copper are presented. The samples with induced stresses of 9.4 and 10.2 MPa were compared to a substrate with no load and were held at 25 °C and 10% relative humidity for 600 hours. As is evident from the micrographs, whisker formation occurred in all cases with a slight increase in frequency of the loaded samples as compared to the 0 MPa control. The concentrations of whisker formation are shown in Table 1.

Samples tested to determine the environmental effects on whisker formation were held for a considerably longer time than the samples in the bend test study. Tin films were electrodeposited on copper substrates at the University of South Carolina and were exposed to gases at pressures of 0, 0.5, 1 and 4 atm (see Figure 7). The vessels were held for a period of 200 days (4800 hours). The films were characterized and the results are summarized in Figures 8-12. The concentration of whiskers/hillocks was measured and is summarized in Figure 8. No significant difference in concentration is apparent between the air sample and nitrogen. The evacuated samples showed elevated whisker concentrations compared to samples exposed to either air or nitrogen. In addition, when Figure 9-12 are studied, it is evident that the whiskers that formed in the evacuated vessels longer whiskers in comparison to the higher absolute pressures. The samples held at higher absolute pressure appear to grow more slowly.



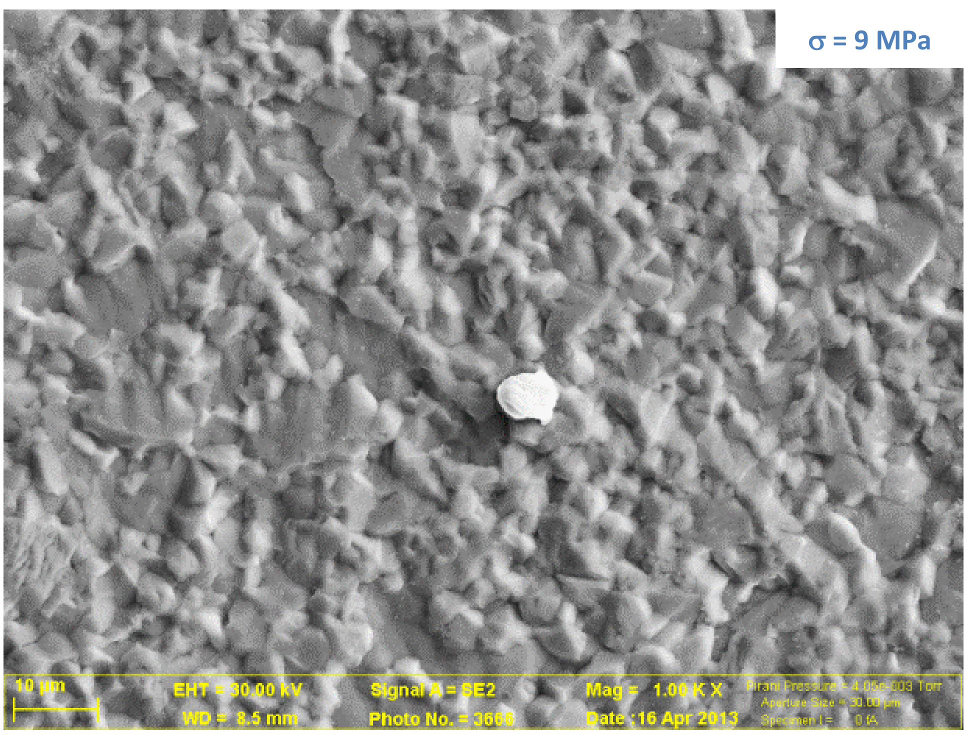
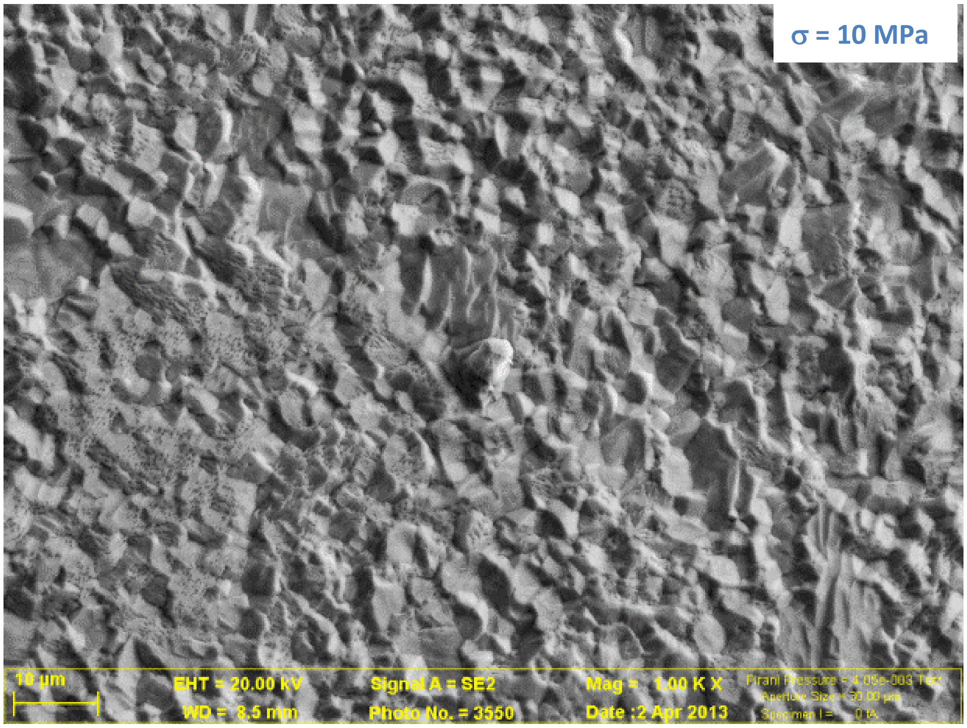


Figure 5: Four-point Bend Test Results of Sn film on Cu Substrates at Various Stress Levels after 770 hrs



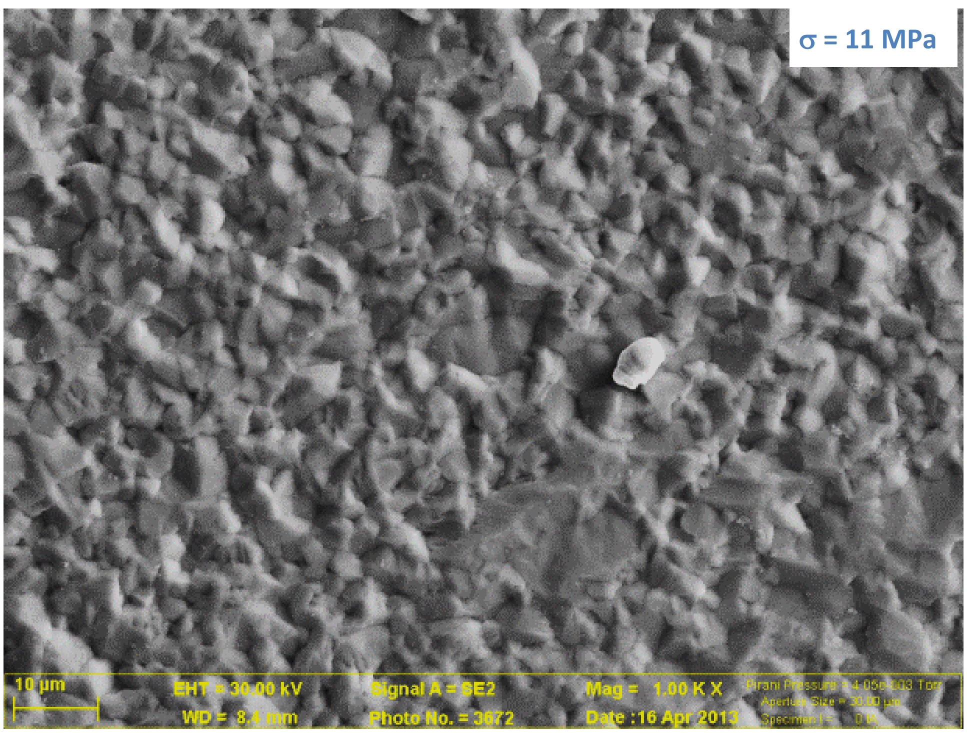


Figure 5 (continued): Four-point Bend Test Results of Sn film on Cu Substrates at Various Stress Levels after 770 hrs

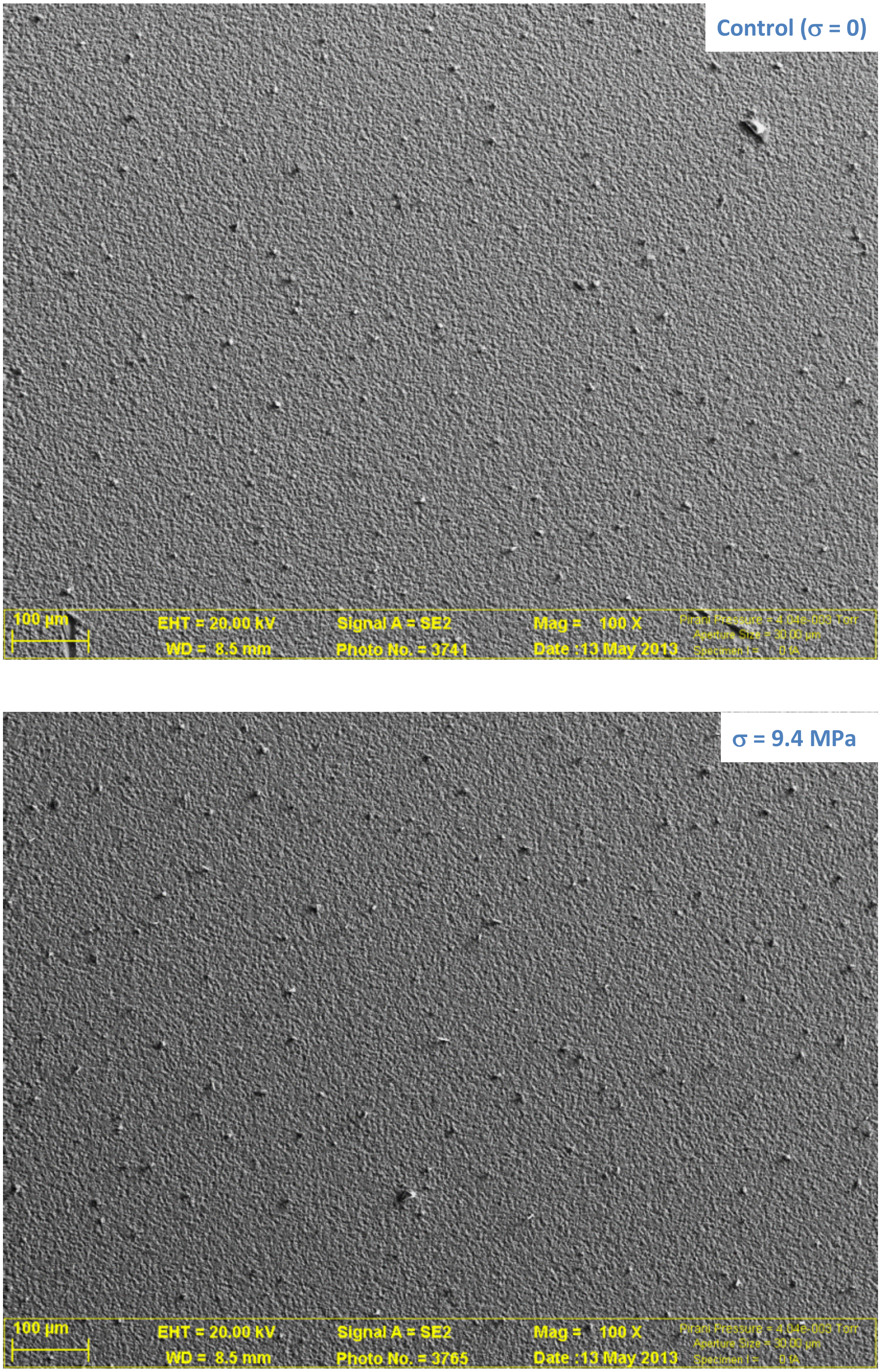


Figure 6: Four-point Bend Test Results of Sn film on Glass Substrates at Various Stress Levels after 600 hrs

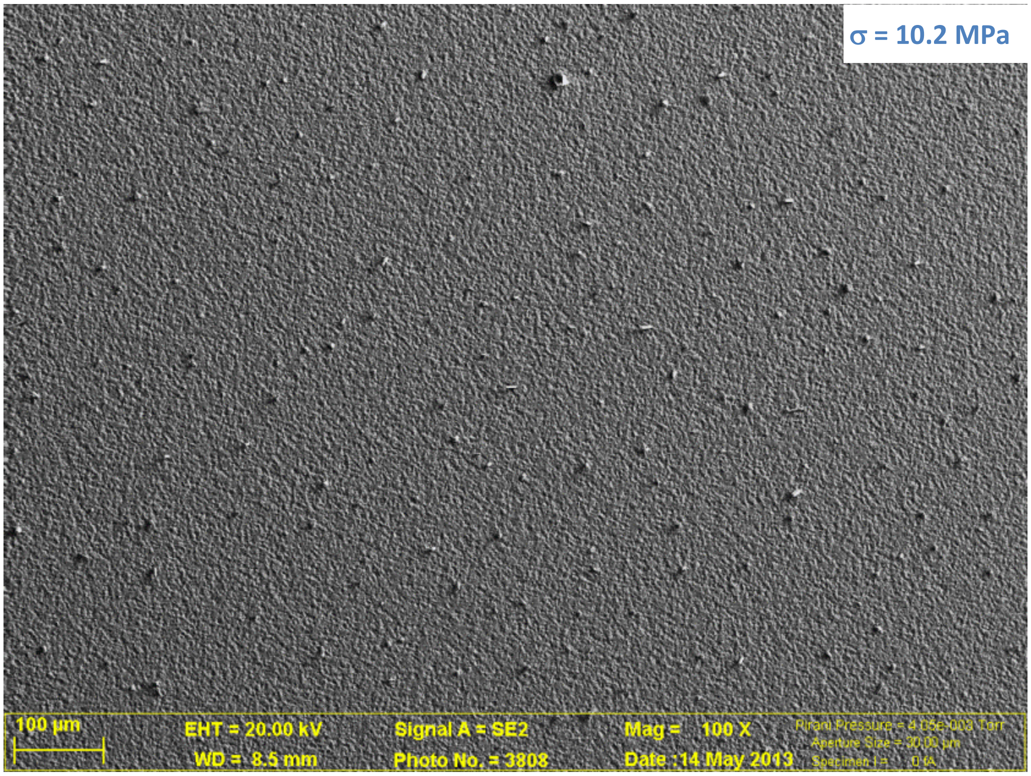


Figure 6 (continued): Four-point Bend Test Results of Sn film on Glass Substrates at Various Stress Levels after 600 hrs

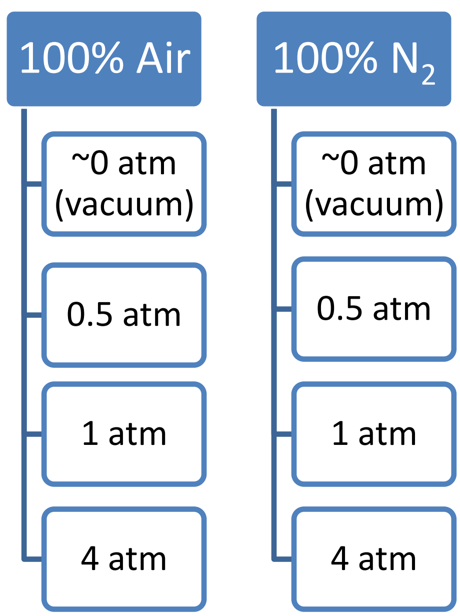


Figure 7: Matrix of Environmental Test Performed at Ambient Temperature

Table 1: Concentration of Bend Tests of Sn film on copper coated Glass Substrates at Various Stress Levels after 600 hrs

Stress (MPa)	Concentration (Whisker/mm^2)
0	182.7
9.4	262.1
10.2	257.9

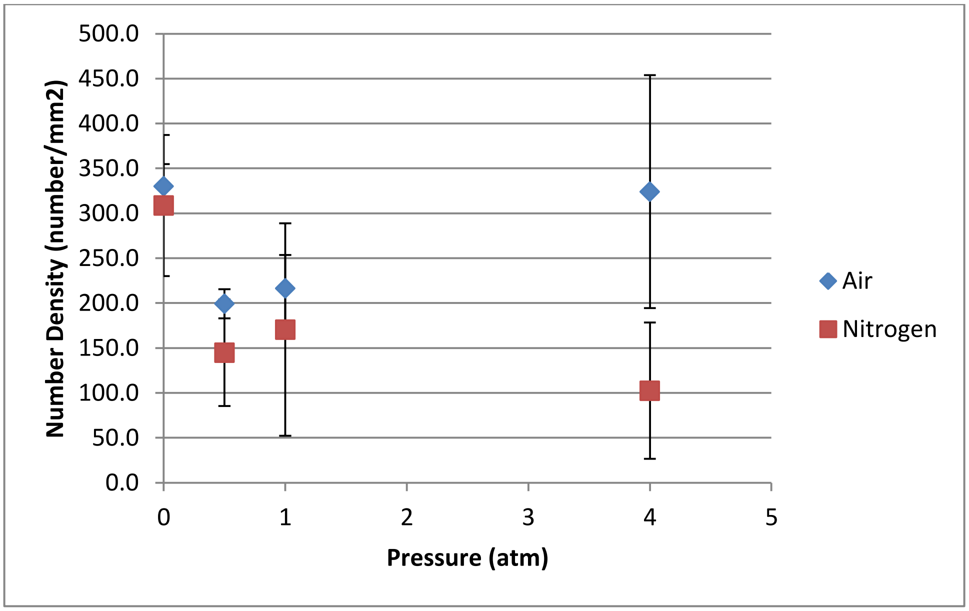
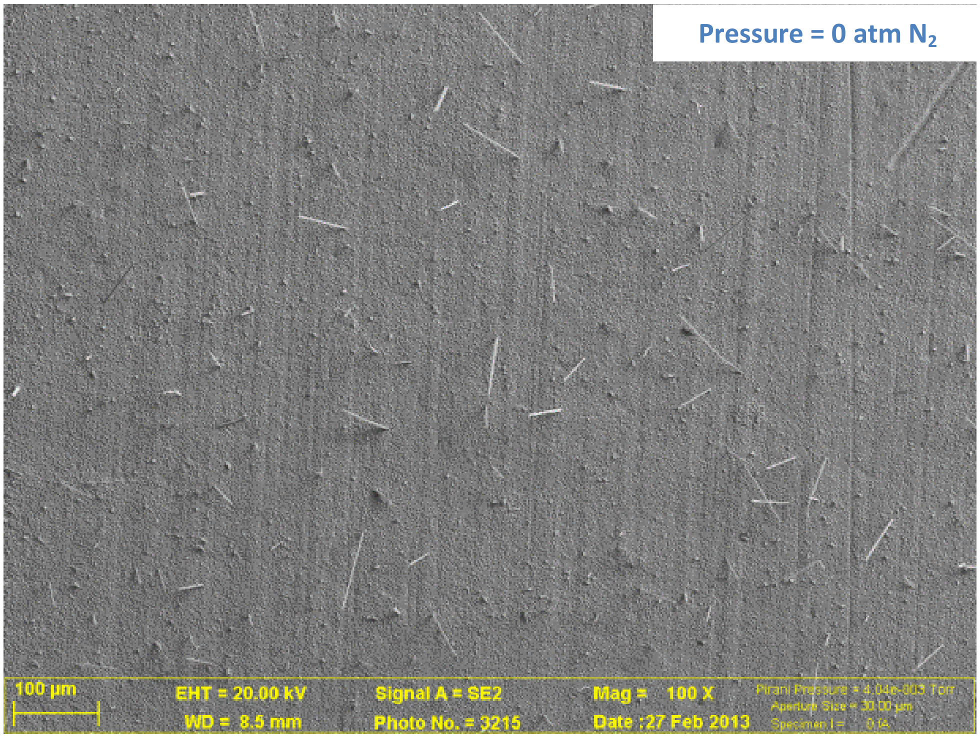


Figure 8: Number Density of Whisker/hillock appearance after ~200 days in the gaseous environment at various pressures



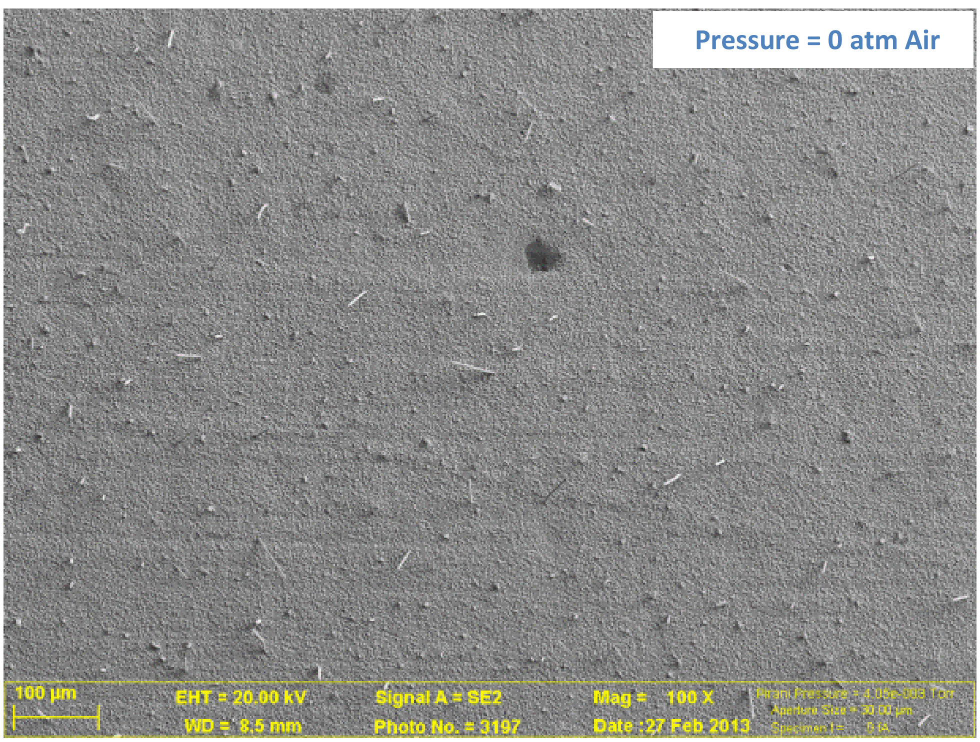
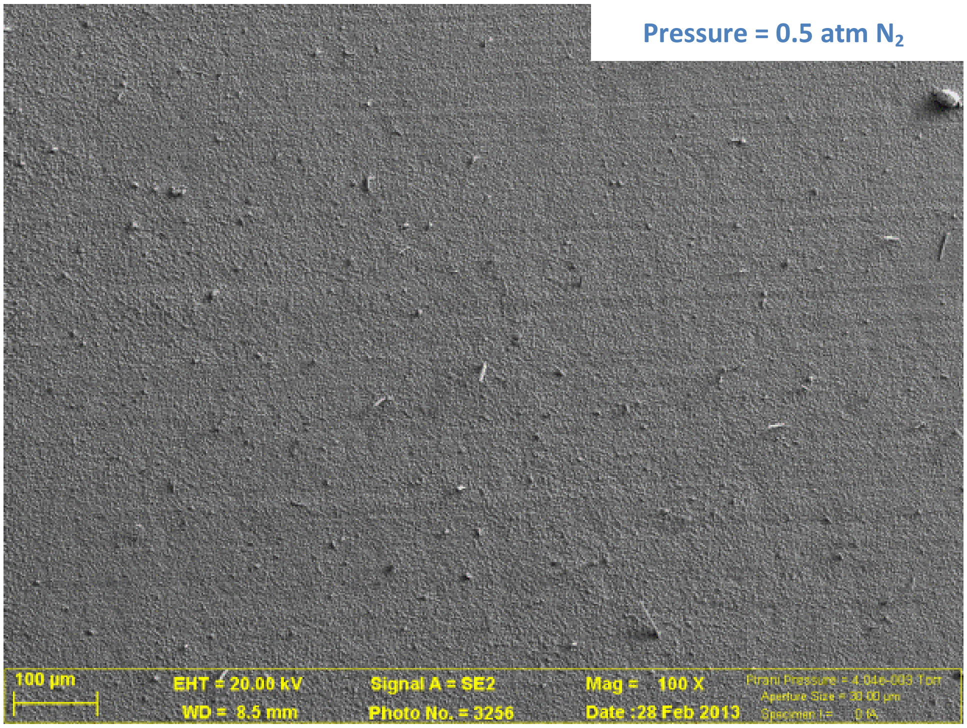


Figure 9: Environmental Testing of Sn film on Cu Substrates under Vacuum (0 atm) for 5200 Hours



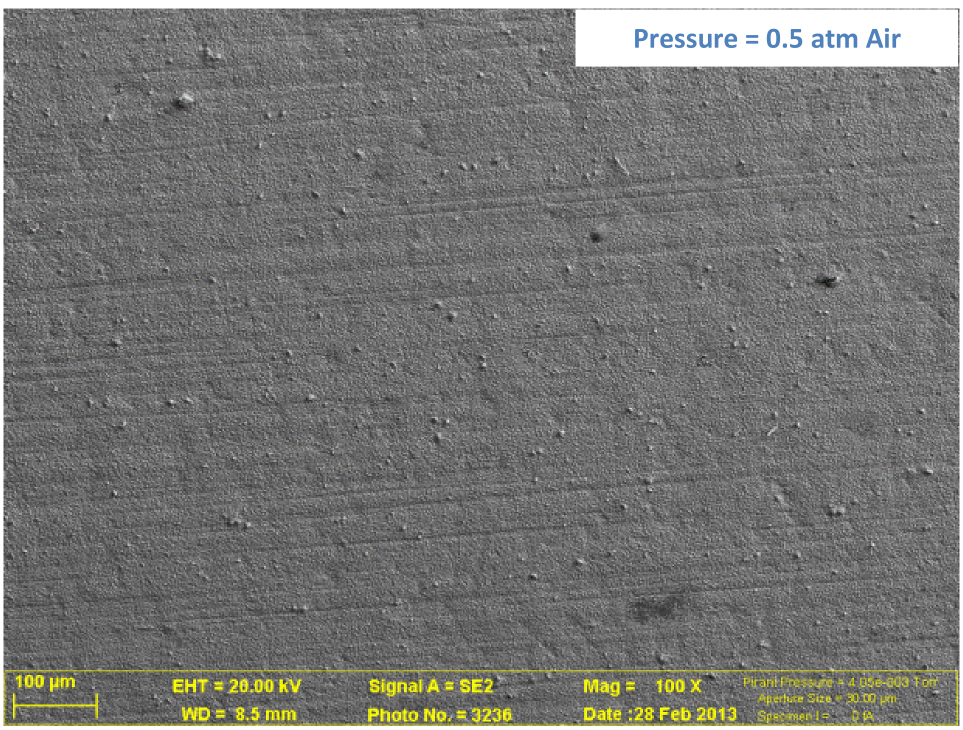
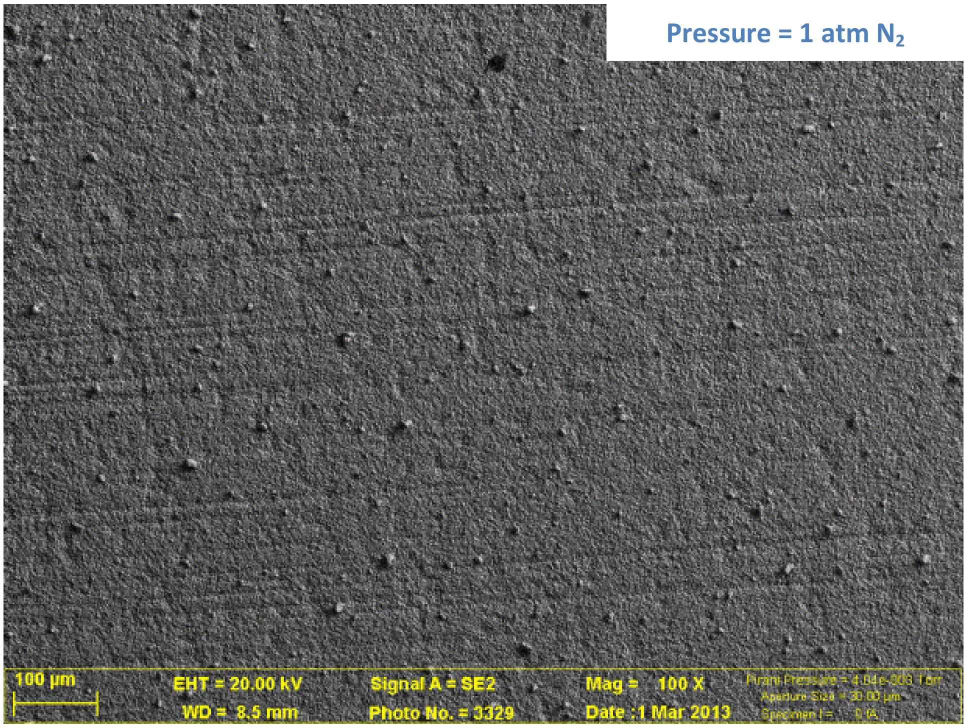


Figure 10: Environmental Testing of Sn film on Cu Substrates under 0.5 atm for 5200 Hours



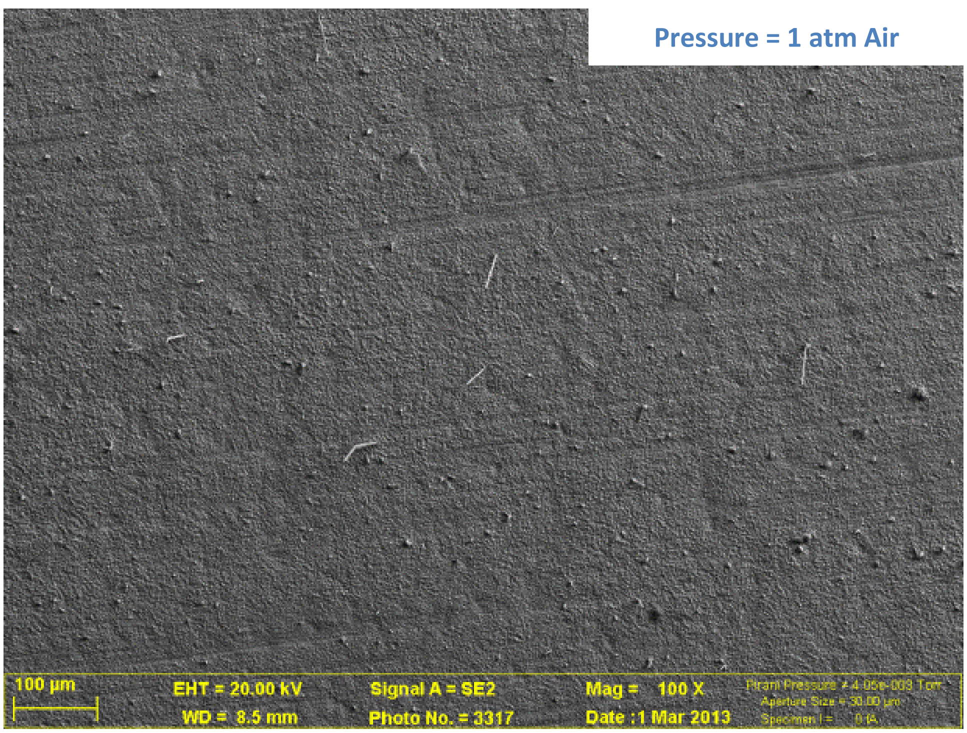
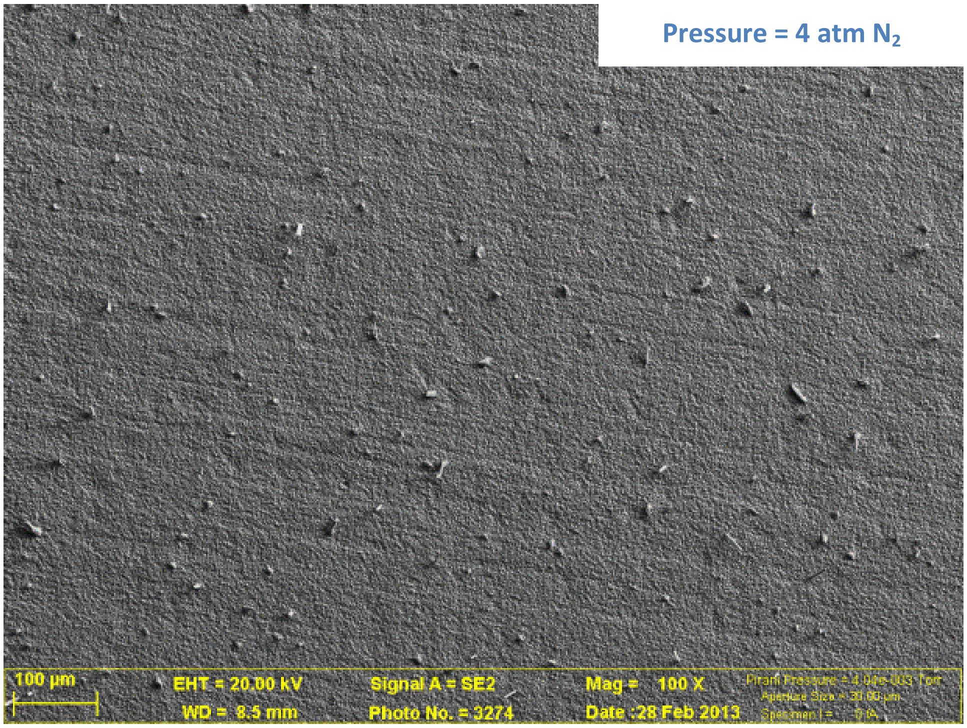


Figure 11: Environmental Testing of Sn film on Cu Substrates under 1 atm for 5200 Hours



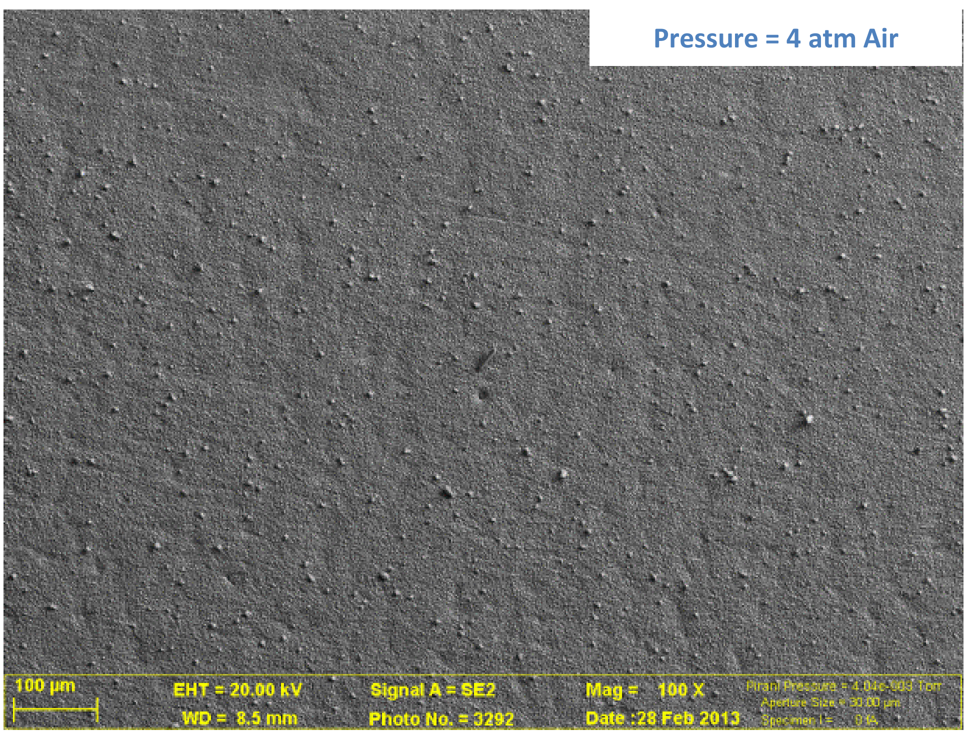


Figure 12: Environmental Testing of Sn film on Cu Substrates under 4 atm for 5200 Hours

Discussion

The results of the four-point bend tests did not yield a trend linking the degree of stress (9-11 MPa) applied to the sample corresponding to the number, length, or morphology of whisker growth. As previously stated, the stress state of the films is a result of several internal (e.g., formation of intermetallic compounds) and external (e.g., applied load) factors [4]. The tin on copper samples exhibited very slow rates of whisker formation at all levels of externally applied stress including the control (0 MPa). The tin on glass (with 300nm film of Cu) samples exhibited much higher rates of whisker formation. This observation was also noted in the control sample (0 MPa). Although those samples that were loaded showed a moderate increase in whisker concentration, this may not be significant. Further testing would be needed to conclude an actual difference.

Alternatively, the different substrate materials of each sample set could have resulted in different levels of residual stress induced in the tin film which may account for the apparent insensitivity of whisker density to bend stress. No residual stress measurements were conducted in the films but previous studies [9, 10] have shown that these stresses can affect whisker growth. Hence, it is suggested that further studies of this nature measure the stress in the film, as soon as it is deposited, with and without loading. This information may prove invaluable to understanding the role of these phenomena in whisker growth.

Environmental testing studied the effects of oxygen content on whisker nucleation and growth. There is apparently not a significant effect of oxygen partial pressure on whisker density and growth. However, lower absolute pressures did exhibit higher whisker densities of large aspect ratio. It is not understood why the initial observations [1] were not confirmed in the present experiments. One potential reason could be the condition of the initial layer of tin oxide. It has been proposed that tin oxide plays a role in whisker growth [11]. Tu stated that whiskers grow at weaker spots on the tin surface where the surface oxide has been broken and whisker growth relieves local stresses in the tin film. Oxide films on tin have been observed to form immediately after exposure to air and grow faster in humid conditions than dry air [12]. The current study did not address the condition of the initial surface oxide prior to exposure in air/nitrogen atmospheres. In addition, it has not been determined if the environmental atmosphere during the test would cause a breakdown in the surface oxide or allow the oxide to reform if cracks were present during exposure. If discontinuities in the oxide layer lead to initiation of whiskers, then an understanding of oxide stability in the environment is vital to discern the impact of oxygen partial pressure on whisker growth. This is suggested for further study.

Conclusions

The environmental factors influencing formation of tin whiskers on electrodeposited tin coatings over copper substrates was examined in the present study. The effect of stress on the nucleation and growth of whiskers was studied. The results show that induced compressive stresses increase the concentration of whiskers, slightly. However, the residual stress state in the film was not directly measured and could vary due to several factors. It is recommended that further studies on this subject measure the residual stress in the film prior to testing.

The effect of oxygen content was also studied by aging substrates in gas vials of varying absolute pressures and different levels of oxygen. The growth of whiskers/hillocks appears to be inversely proportional to absolute pressure but is less sensitive to oxygen partial pressure, as observed in the interim report. This observation underscores the stochastic nature of these experiments. It is recommended that further studies characterize the oxide layer prior to exposure. This is vital to discern the influence environmental factors on the initiation and growth of whiskers.

References

[1] E. N. Hoffman, P. S. Lam and X. Li, "Interim Report: Contributions of Stress and Oxidation on the Formation of Whiskers in Pb-free Solders," WP-1754
[2] George T. Galyon. "A History of Tin Whisker Theory: 1946 to 2004," IBM eSG Group, SMTAI International conference, September 26-30, 2004 (Chicago, IL)
[3] R.M. Fisher, L.S. Darken, and K.G. Carroll,"Accelerated Growth of Tin Whiskers," *Acta Metallurgica*. 2(3): pp. 368-372, May 1954
[4] B.Z. Lee and D.N. Lee, "Spontaneous Growth Mechanism of Tin Whiskers," Acta Metallurgica, 46(10): pp. 3701-3714, 1998
[5] Y. Wang, Purdue University, personal communication, May, 2013
[6] Standard Test Methods for Bend Testing of Metallic Flat Materials for Spring Applications Involving Static Loading, ASTM E855 − 08
[7] Standard Test Methods for Flexural Strength of Advanced Ceramics at Ambient Temperature, ASTM C1161− 02
[8] Mechanics of Materials, F. P. Beer & E. R. Johnston McGraw-Hill Book Company, New York, NY 1981
[9] 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)
[10] Y. Sun, E. N. Hoffman, P-S. Lam and X. Li, "Evaluation of local strain evolution from metallic whisker formation," Scripta Materialia 65 (2011) 388–391
[11] K.N. Tu, "Irreversible Processes of Spontaneous Whisker Growth in Bimetallic Cu-Sn Thin Reactions," Phys. Rev. B, 49(3): pp. 2030-2034, January 1994
[12] S. Cho, J. Yu, S. K. Kang, and D.-Y. Shih, "Oxidation Study of Pure Tin and Its Alloys via Electrochemical Reduction Analysis," Journal of ELECTRONIC MATERIALS, 34, No. 5, 2005

Appendix A: Interim Report

Contributions of Stress and Oxidation on the Formation of Whiskers in Pb-free Solders

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Objective

The objective of this project is to increase the understanding of the role of stress and oxide formation on whisker growth in lead-free solders. This understanding will support the development of a predictive model, enabling engineers to design solder alloys for whisker growth resistance.

Technical Approach

Sample Preparation

Sn and SnPb thin films on Cu substrates were fabricated by electrodeposition in an electrochemical workstation (model 760D, CH Instruments, Austin, TX) with a three-electrode system. A titanium-mesh electrode with 10 µm thick platinum film was used as the counter electrode and the reference electrode was Ag/AgCl. Chemicals of analytical grade and double-distilled water were used throughout all experiments. For Sn deposition, sodium citrate tri-basic di-hydrate ($C_6H_5Na_3O_7 \cdot 2H_2O$) was added into a tin (II) chloride ($SnCl_2 \cdot 2H_2O$) aqueous solution to achieve a stable stannous solution. A constant current density, 4 mA/cm^2, was applied to reach a homogenous and continuous thin film. Uniform coatings of SnPb (~50 wt% Sn and ~50 wt% Pb) were obtained with a methane-sulfonic acid (MSA) based bath with addition of tin (II) methanesulfonate ($(CH_3SO_3)_2Sn$) and lead nitrate ($Pb(NO_3)_2$). Chronopotentiometry deposition method with a cathodic current density of 20 mA/cm^2 was used during deposition. All the samples have a spherical grain feature, which was typical for electrodeposition. The thickness of the samples was measured to be approximately 10 µm in the middle of the samples. Such thin thickness is stated to be a precondition for observable whisker growth. The cross-section image also demonstrates a good bonding between the deposited films and the substrates.

Oxygen analysis

The technical approach described in the original proposal involved utilizing a Sable Systems Oxzilla II dual cell respirometer oxygen analyzer to monitor the potential oxidation reaction fueling the compressive stress for whisker growth. The oxygen analyses eventually led to utilizing an atom probe to look for the presence of oxygen subsurface.

To determine if oxygen content within the surrounding atmosphere had some effect on whisker growth, a series of valved mini-conflat flange vessels loaded with samples were prepared with various ratios of air to nitrogen: 100% air; 25% N_2/75% air, 50% N_2/50% air, 75% air/25% N_2, and 100% N_2.

Stress State

In addition to oxidation evaluate, the original proposal outlined that stress was to be calculated by measuring strain via laser curvature method. The stress state of the lead-free solder film deposited on a substrate may be obtained by measuring the curvature of the specimen then applying the classical Stoney equation published in 1909. In the late 1990s, Freund derived the formula based on Kirchhoff thin plate theory with an energy method, which allows a straightforward extension to the more complex multilayer systems. It was noted that Stoney equation remains a simple and effective method to evaluate thin film stresses even more advanced equipment is now available. However, the use of Stoney equation may be subject to two major disadvantages: 1) the specimen curvature must be measured reliably for these very thin specimens; and 2) only global uniform background stress in the film can be obtained. Therefore, the overall average stress of the sample may be estimated, but the local stress that initiate a whisker to form, or the local stress perturbation due to the growth of a whisker or a hillock, or cannot be obtained directly.

Early on in the experimentation, it was found that whiskers were growing sporadically over the surface of the samples opposed to evenly across the surface. Measuring a global strain utilizing the laser curvature method did not appear to be the most accurate way of monitoring the stress state resulting in whisker growth as whiskers were not growing evenly across the surface yet the laser method would be measuring an average surface stress.

An effort to evaluate the strain at a local level led to the utilization of digital image correlation (DIC) to evaluate the strain locally around a formed whisker. The digital image correlation (DIC) was used to measure the thin film strain distribution and its revolution as the surface feature is changing. Through pixel-by-pixel comparison of the initial (as deposited) morphology with the subsequent images in the same area of interest, the surface displacement can be obtained, from which the local strains are calculated for the post-formation of the whiskers or hillocks can be obtained. A proper constitutive relation for the film is required to relate the deformation to the stress.

The distinct spherical characteristics of thin film morphology can be used in place of an artificially applied speckle pattern without further modification on the sample surface. This unique feature is especially advantageous for the current application with DIC, since the artificial patterns or gratings will obscure the observation of local whisker activities. A series of images on identical locations of the samples were taken with SEM (Quanta 200, FEI) using a constant voltage of 30 kV and a constant spot size of 5 μm in consecutive sessions, before and after whiskers were visually present. Resolution of the images was held constant at 1024×968 pixels. During intervals between the contiguous SEM sessions, which ranged up to ~20 days, the samples were kept at ambient environment (~23 °C and ~30-60% relative humidity or RH without controlling the ambient atmosphere). An array of Vickers indentation marks was made at different locations. These depressed sites served as an additional source of compressive stress/strain in addition to the residual stress from film deposition, and as markers to identify the areas of observation during the SEM sessions.

A finite element model was applied to solve for the detailed stress and deformation fields for the thin film/coating system by using the DIC measured surface displacements as the boundary condition. The elastic-plastic nonlinear analysis is required because the thin film is expected to be in a large deformation state to accommodate the presence of whiskers or hillocks.

Constitutive relations used in the model include:

(1) Linear Elasticity

The general Hooke's Law in tensor notation can be written as:

$$\sigma_{ij} = \frac{E}{1+\nu}\varepsilon_{ij} + \lambda\varepsilon_{kk}\delta_{ij}$$

$$\lambda = \frac{\nu E}{(1+\nu)(1-2\nu)}$$

where σ_{ij} are stress components, ε_{ij} is the (total) strains, E is the Young's modulus, ν is the Poisson's ratio, λ is the Lamé's constant, the subscript index (e.g., i or j) ranges from 1 to 3 (1= x, 2= y, and 3= z), and δ_{ij} is the Kronecker delta:

$$\delta_{ij} = \begin{cases} 1, \text{ if } i = j \\ 0, \text{ if } i \neq j \end{cases}$$

The repeated indices indicate summation:

$$\varepsilon_{kk} = \varepsilon_{11} + \varepsilon_{22} + \varepsilon_{33} = \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}$$

which is the hydrostatic part of the strain.

The calculations with the actual DIC displacement measurement indicated that the elastic solution is impractical due to the very high in-plane stresses (in the order of GPa). Therefore, the elastic-plastic formulation must be pursued.

(2) Elasto-plasticity with Isotropic Strain Hardening (Incremental Plasticity)

Based on von Mises yield criterion, when a stress state satisfies:

$$\overline{\sigma} = \sqrt{\frac{3}{2}s_{ij}s_{ij}} \; > \; \sigma_o$$

however, the linear elasticity is no longer valid. In the above equation $\overline{\sigma}$ is Mises stress (i.e., equivalent stress or effective stress), σ_o is the initial yield stress, and s_{ij} is the deviatoric stress defined by:

$$s_{ij} = \sigma_{ij} - \frac{1}{3}\delta_{ij}\sigma_{kk}$$

With the associated flow rule, the Prandtl-Reuss equation to relate the strain increment to the stress increment becomes:

$$\dot{\sigma}_{ij} = \frac{E}{1+\nu}\left[\frac{\nu}{1-2\nu}\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jll} - \frac{1}{1+\frac{h}{3G}}n_{ij}n_{kl}\right]\dot{\varepsilon}_{kl} \qquad (1)$$

where the dots represent the rate or increment, the normal n_{ij} is defined as $n_{ij} = \frac{s_{ij}}{\sqrt{s_{kl}s_{kl}}}$, h is the tangent modulus (local slope) of the stress-plastic strain curve ($h = \frac{d\overline{\sigma}}{d\overline{\varepsilon}^p} = \frac{\dot{\overline{\sigma}}}{\dot{\overline{\varepsilon}}^p}$), the equivalent plastic strain rate is $\dot{\overline{\varepsilon}}^p = \sqrt{\frac{2}{3}\dot{\varepsilon}_{ij}^p\dot{\varepsilon}_{ij}^p}$, and $\dot{\varepsilon}_{ij}$ is the “total” strain increment that is the sum of elastic and plastic strain increments (the superscript indicating plastic part).

Note that the condition h= 0 corresponds to elastic-perfectly plastic material (nonhardening), which may be used to approximate the soft solder materials such as tin (Sn) if the full stress-strain curve is unavailable. The first two terms in Eq. (1) are for the elastic strain increment and the third term is the plastic portion of the strain increment.

The general purpose finite element program ABAQUS has built-in constitutive relations such as those described above. In the present analysis, the incremental plasticity formulation was adopted (Eq.(1)).

<u>Materials Properties</u>:

(1) Copper Substrate

The linear elastic material properties were used. The Young’s modulus is 124 GPa and the Poisson’s Ratio is 0.33.

(2) Coating – Tin Thin Film

The Young’s Modulus is 41 GPa, the Poisson’s Ratio is 0.33, the Yield Stress is 11 MPa, and the Elongation at Break is 0.57 (25 mm gage)

(3) Intermetallic Compound (Cu_6Sn_5)

The Young's Modulus is 85.56 GPa and the Poisson's Ratio is 0.309. Only elastic properties are available.

Three-dimensional Finite Element Model

Only a small strip of the Sn-Cu system was modeled. The dimensions are shown in Figure 1. The thickness of the intermetallic compound was chosen to be 0.5 μm based on the experimental results. The finite element mesh can also be seen in Figure 1, for which 43,164 elements with 47,520 nodes were used.

Boundary Conditions

The bottom of the model (Cu substrate) was fixed in space. The DIC surface displacements were imposed, as representatively shown by the strain distribution, Figure 1.

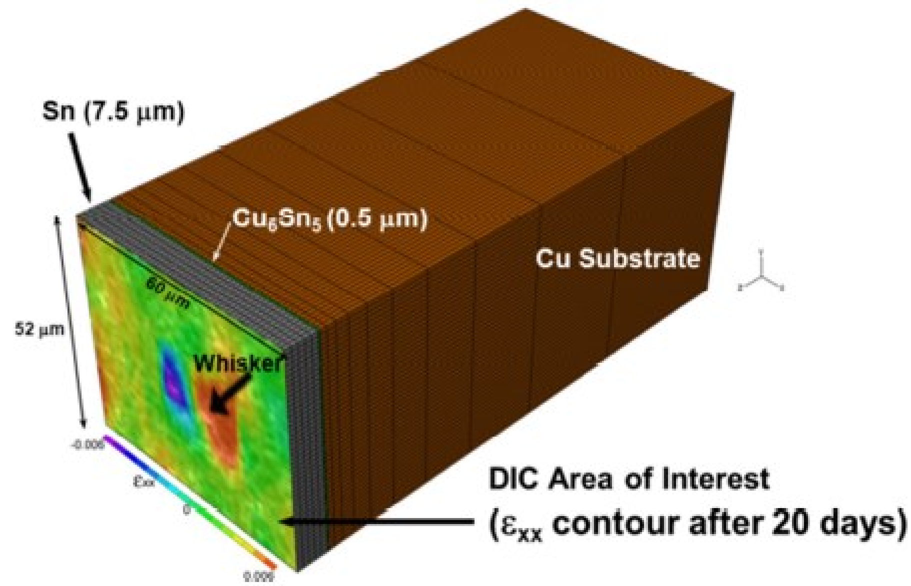

Figure 1 Illustration of area of interest for digital image correlation.

The application of external stress was described in the original proposal to include gamma radiation and mechanical bending. Both gamma radiation utilizing a Co-60 cell and mechanical bending experimentation were started early to determine the effect of the external stress on whisker growth.

It was recognized that the strain measurement obtained through DIC was a surface measurement, and the stress leading to whisker formation is expected to reside subsurface. In an attempt to evaluate the subsurface strain, X-ray tomography was utilized to obtain X-ray images subsurface in an attempt to apply DIC.

Gamma Irradiation

A series of Sn thin films electrodeposited onto Cu substrate, prepared using same synthesis methods, was exposed to two different Co-60 gamma fluxes and a control was unirradiated. The unirradiated sample grew whiskers. The samples exposed to the gamma radiation did not grow whiskers, but formed deposits of $Cu_2NO_3(OH)_3$ on the surface (Sn film). The presence of this compound most likely is due to the radiolysis of nitrogen containing air. The amount of deposits varied depending on the radiation flux. The lower flux resulted in larger amounts of $Cu_2NO_3(OH)_3$. The higher flux resulted in smaller amounts of deposit. The difference in deposit amount may be a result of the difference in radiation flux, or possibly due to the volume of air in the chamber. Note that two very different radiation chambers were used for experimentation to provide the different flux values.

Mechanical Bending

A series of mechanical bending tests were developed to test Sn on Cu systems in elastic and plastic stress states. A clamp jig was fabricated to hold samples in varying degrees of bending and to be loaded into an SEM without removing the samples from the mechanical bending stress, see Figure 2.

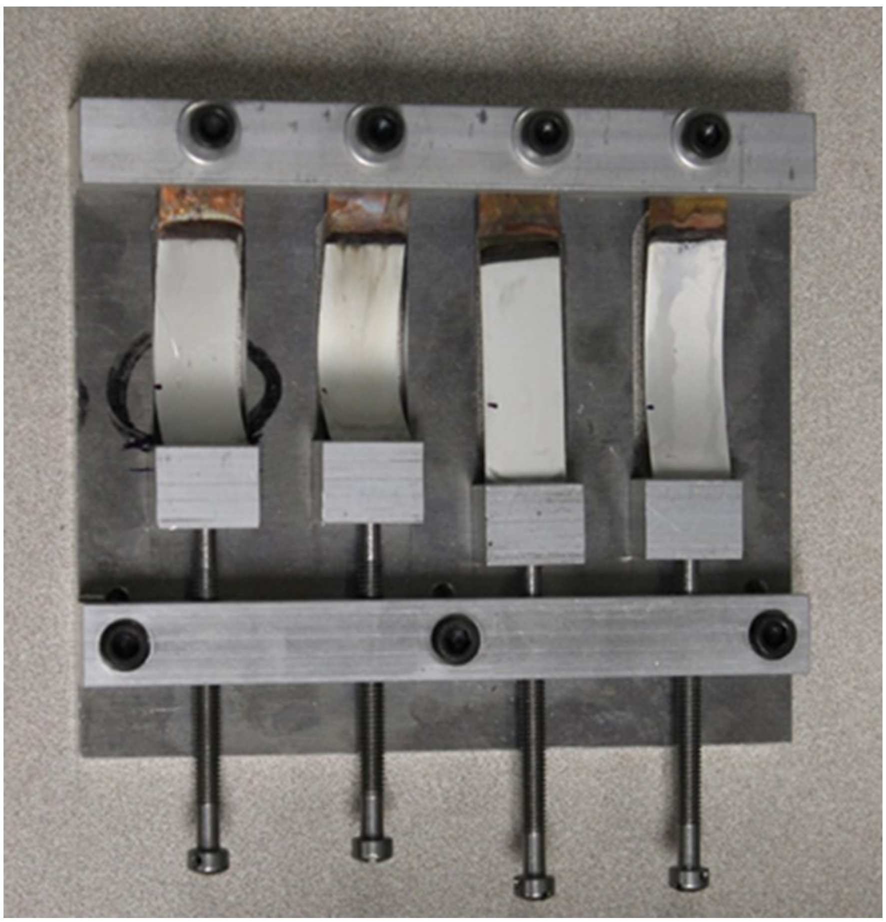

Figure 2 Mechanical bending jig with samples loaded at varying bending curvatures.

Results and Discussion

Sample Preparation

Single Layer Thin Films

Samples were prepared with consistent coatings of Sn, SnPb, and SnBi, see Figure 3.

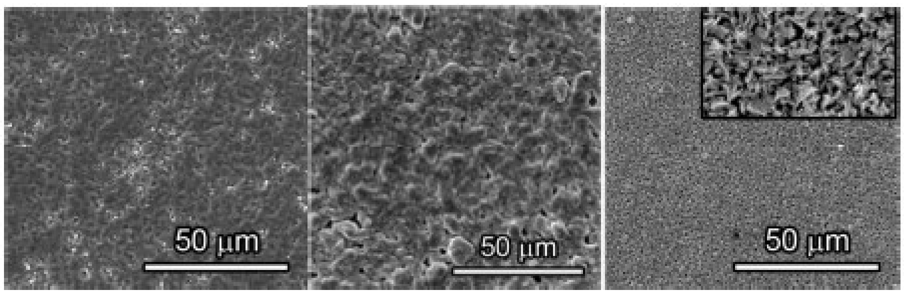

Figure 3 Thin film coatings on copper substrate (left) Sn, (center) SnPb, (right) SnBi

Dual Layer Thin Films

Dual thin films were also achieved on Cu substrate. The most successful one is the SnPb/Sn/Cu sample. Due to the smooth morphology of the first Sn layer, the final SnPb layer was almost as good as the simple SnPb on Cu samples, see Figure 4.

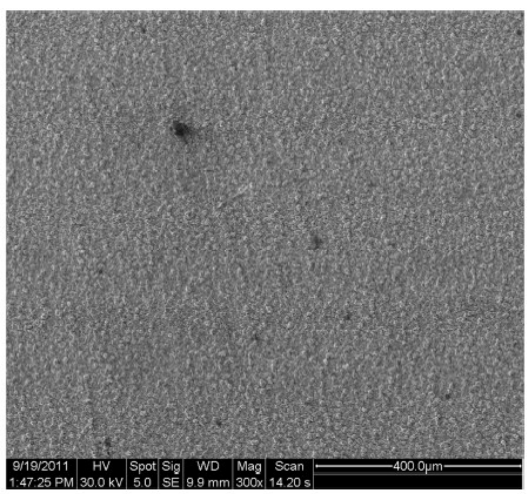

Figure 4 Typical Sn/SnPb/Cu sample morphology.

For Sn/SnPb/Cu sample, Figure 5, refiner was used when first deposit SnPb alloy on Cu substrate in order to reduce the roughness of the thin film. Otherwise the quality of the final product is not adequate.

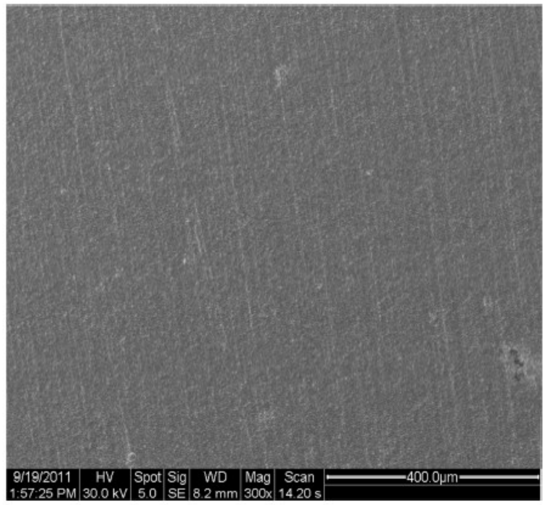

Figure 5 Typical SnPb/Sn/Cu sample morphology.

Oxygen Analysis

Based on both the oxygen analyzer and the atom probe studies, no evidence was found to suggest that oxide formation within the thin film leads to a buildup of compression stress leading to whisker growth.

O2 analyzer

O2 analyzer results after a period of 120 days with a Sn thin film sample under closed vessel proved to be comparable to the reference vessel, which was empty. This result suggests that either oxygen is not being continuously absorbed or that the instrument, with its resolution of 1ppm, noise of <8ppm pk-pk, and drift of <0.02%/24hr, is not sensitive enough to pick up on the absorption.

Atom Probe

Atom probe studies did not find evidence of oxide formation within the bulk of the sample, see Figure 6 and 7. The small amount of oxygen measured through the study was found on the surface of the atom probe samples, most likely due to surface absorption during sample preparation. The atom probe studies did, however, find evidence of platinum throughout the bulk of the sample. The platinum was not detected during the TEM studies due to concentration limits, however, the atom probe was able to confirm the presence of platinum. It can be deducted with reasonable certainty that the platinum source was the counter electrode during the deposition process and that contamination occurred through the electrolyte solution.

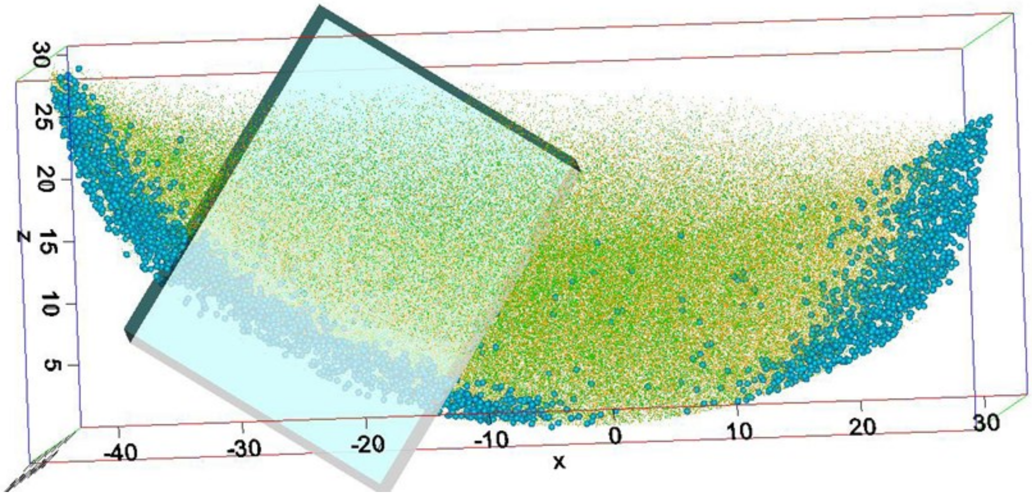

Figure 6 Atom probe map of elements.

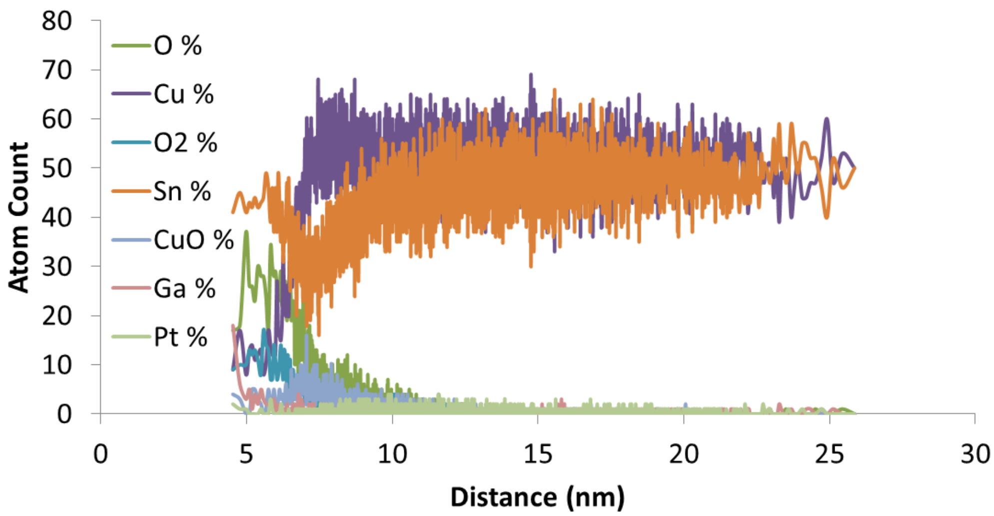

Figure 7 Atom count across area of interest in atom probe sample. Oxygen present at surface then falls to background counts within the sample bulk.

Sealed Vessels

SEM analysis confirmed a difference in whisker growth between samples stored in 100% air and 100% nitrogen for 263 days, see Figure 8. The sample stored in 100% nitrogen had an increased number of whiskers. The whiskers were also longer compared to the samples stored in 100% air. The samples with ratios of air and nitrogen had an intermediate amount of whisker and an intermediate length, relative to the 100% air and 100% nitrogen samples. The result at this time confirms a difference; however, it is too early to state the cause of the difference with certainty. The difference may stem from the lack of oxygen in the nitrogen sample affecting the surface oxide layer, thereby influencing whisker growth. Alternatively, the presence of nitrogen could play a factor in effecting the surface layer. While the overall pressure of the vessels was fairly consistent, the partial pressure of oxygen varied and could influence the results as well. Additional testing on the formed surface oxide will aid in confirming the cause of the difference in whisker growth.

Figure 8 Degree of whisker formation increasing with increasing nitrogen concentration over 263 days.

Stress State

Digital Image Correlation

For the Sn thin film deposited on copper, hillocks/whiskers were visually identified a few days after deposition. In contrast, no observable whisker growth was found on SnPb thin films after a considerable period of time.

The images of the areas of interest were analyzed using a Vic-2D DIC package (Correlated Solutions, Inc., Columbia, SC) software for an incremental correlation. The images taken in the first session were used as reference images (initial state). All other images taken at later times from the same sample were compared to the reference image for constructing the two-dimensional surface in-plane displacement field, from which the strain distribution on the film surface could be calculated. It is well accepted that whisker growth is a diffusion phenomenon driven by residual compressive stress. In the case of a thin film, localized stress state can be easily related to the strain field on the surface, which makes DIC an effective tool for visualizing the progression of stress generation and relaxation, before and after the whisker growth. Since Sn on copper finish had the highest whisker growth rate, majority of the DIC analysis were carried out on pure Sn thin films. Another reason to focus on the pure Sn thin films is that these samples had a relatively flat surface. Since only two-dimensional strain state could be evaluated by the present DIC package, it was necessary to minimize the out-of-plane strains by observing the flat areas if possible.

Finite Element Analysis

The calculated surface strains were compared and verified with the DIC results, as shown in Figure 9. It can be seen that the strain contours are consistent. Note that in ε_{yy} the contour colors are reversed. This is caused by the definition of the Y-axis in the pixel coordinate system which is in an opposition direction with respect to the traditional convention.

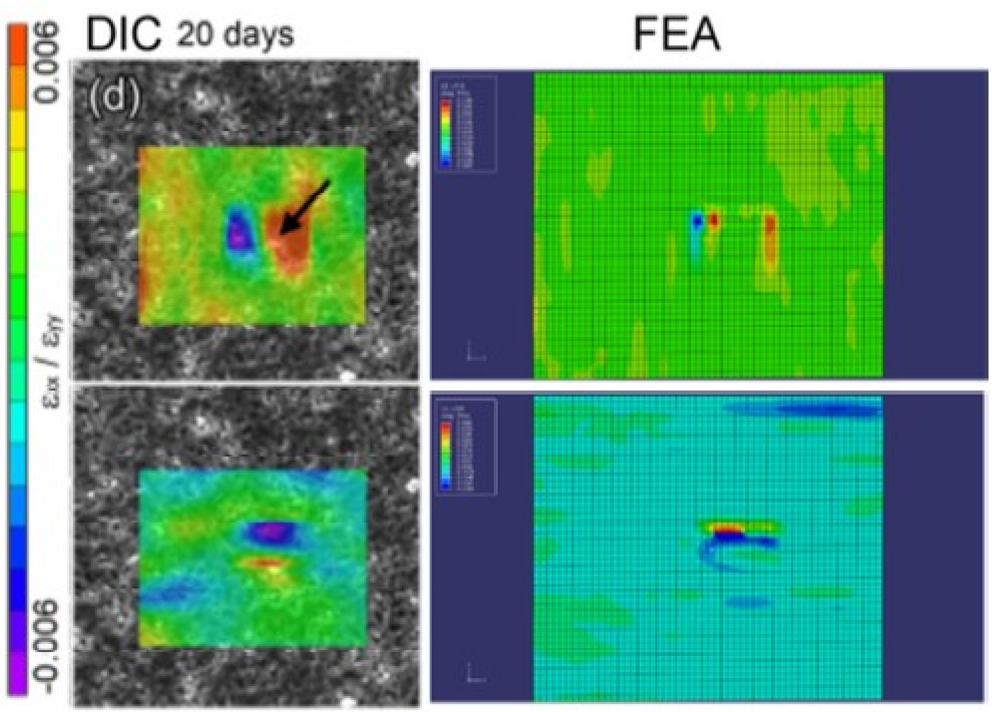

Figure 9 Digital image correlation strain mapping versus finite element analysis mapping.

The stress variation through the tin thin film can be seen ion Figure 10, at which time the specimen has exposed in air for 20 days. Note that the Sn has a total thickness of 7.5 μm; and each sub-layer is 1.5 μm.

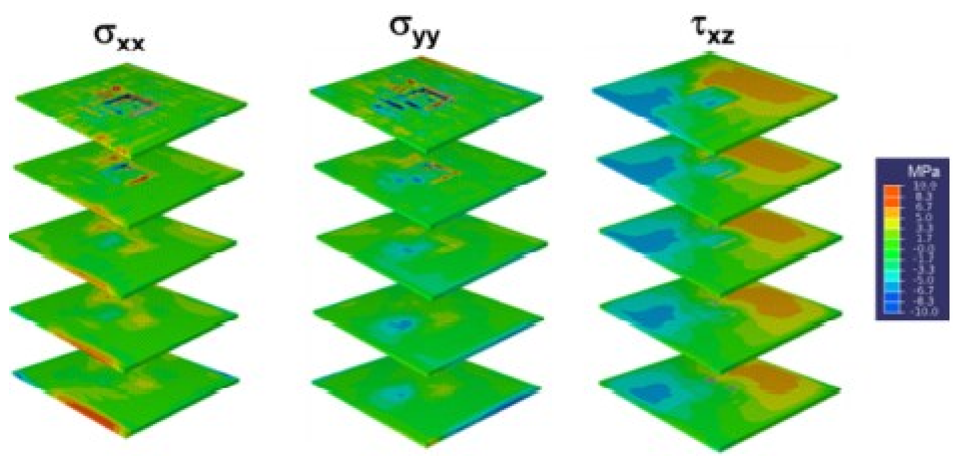

Figure 10 Variation in stress through the coating thickness.

The surface stress history from 1 to 20 days is shown in Figure 11. During the same period of exposure, Figure 12 represents the stresses history immediately above the intermetallic layer (Cu_6Sn_5 total thickness is 0.5 μm; and each sub-layer is 0.25 μm).

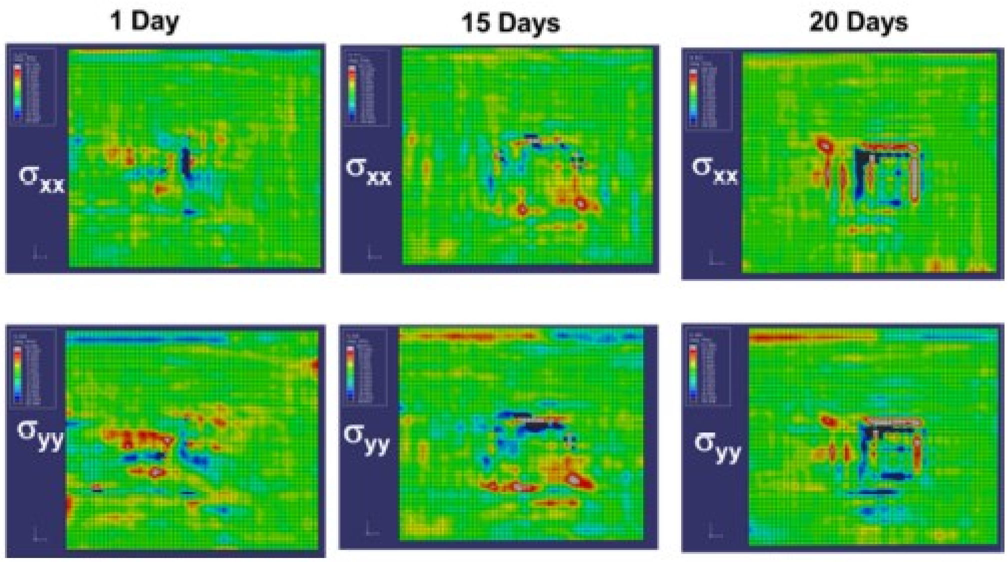

Figure 11 Evolution of surface stress over a 20 day period.

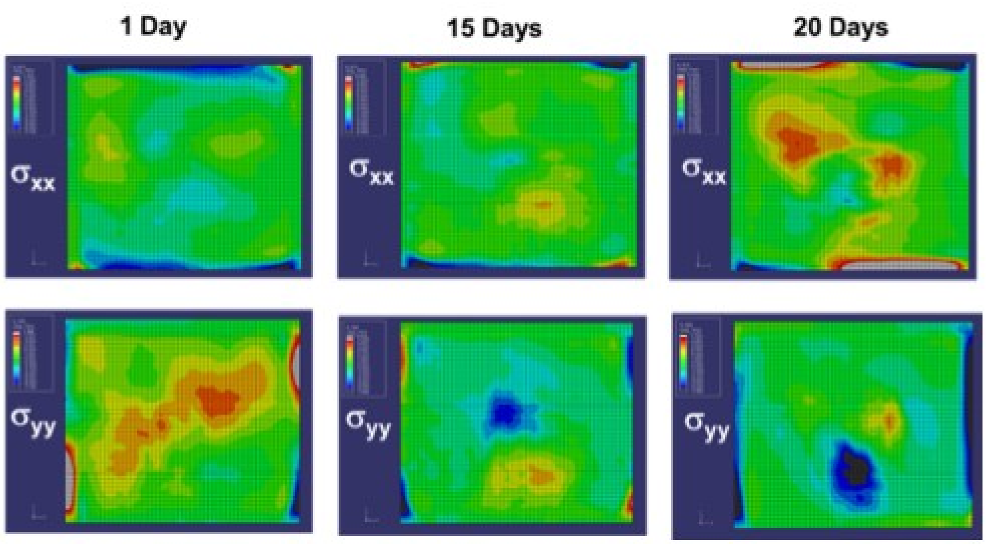

Figure 12 Evolution of stress at the interface over at 20 day period.

Gamma Radiation

Samples were exposed to gamma radiation to determine if radiation would have an influence on the whisker growth rate or degree of whiskering. Experimental results suggest that gamma radiation deters whiskers from forming on in Pb-Sn thin films. The radiation leads to the formation of copper nitrates, $Cu_2(NO_3)(OH)_3$, Figure 13, on the surface of Sn thin films deposited on copper substrates, evidence that copper diffuses through the thin film. Radiation also promotes crack formation within the thin film and can lead to an increased number of low growing hillocks, Figure 14, when compared to unirradiated samples, see Figure 15.

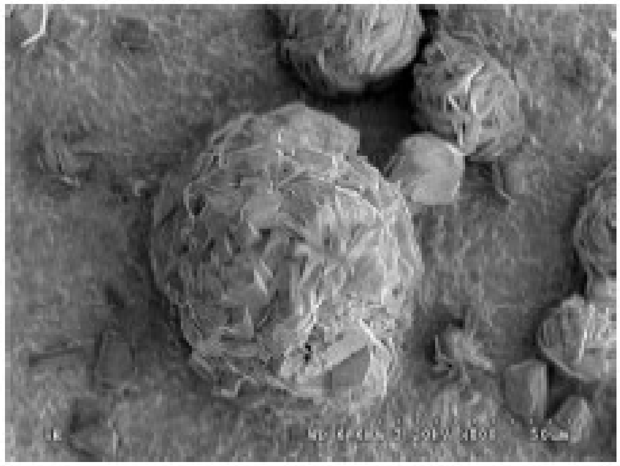

Figure 13 Formation of copper nitrate on surface of gamma irradiated sample.

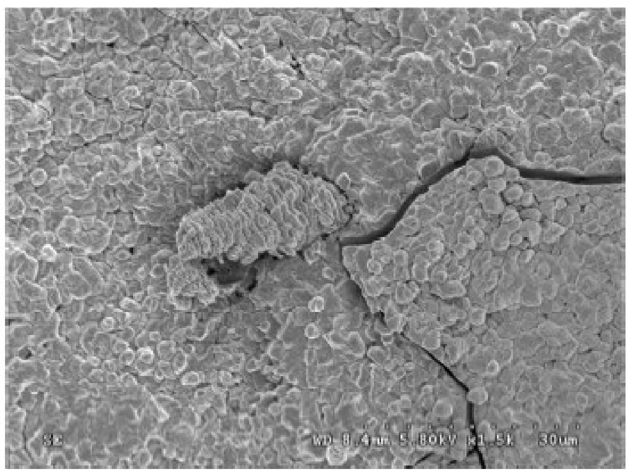

Figure 14 Formation of cracks and hillocks on gamma irradiated sample.

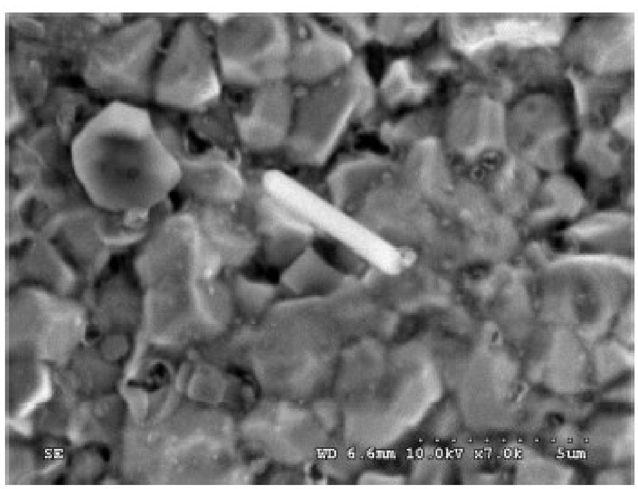

Figure 15 Whisker growing on unirradiated sample from same deposition batch as samples shown in Figures 10 and 11.

Mechanical Bending

On the four sample fixture Sn on Cu samples were bent both elastically and plastically. Below are images showing the growth process after ~100 days. Figure 16 depicts the evolution of the slightly elastically bent sample's surface. No whisker growth was observed in the sample deformed plastically.

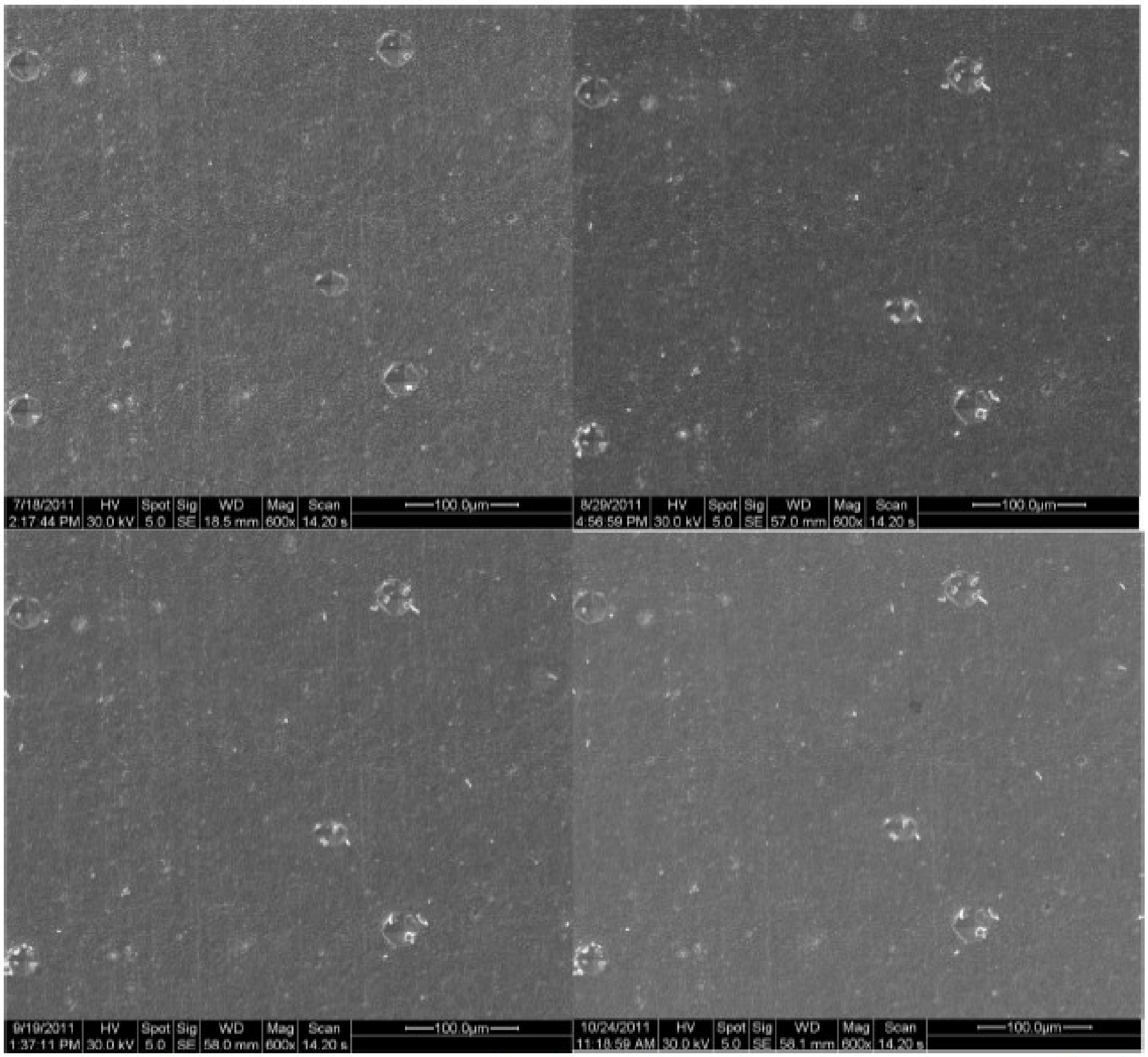

Figure 16 Whisker growth process on the slightly elastic deformed sample. The sequence is a) 7 days; b) 48 days; c) 70 days and d) 100 days after deposition.

In order to prove the validity of the results, a second batch of samples (Sn on Cu) were observed under similar bending condition. No whisker growth is observed on the sample with constant plastic deformation. Two samples with elastic deformation were found to grow whiskers. The sample with larger deflection, i.e. larger elastic deformation, was found to have increased whisker formation, see Figure 17.

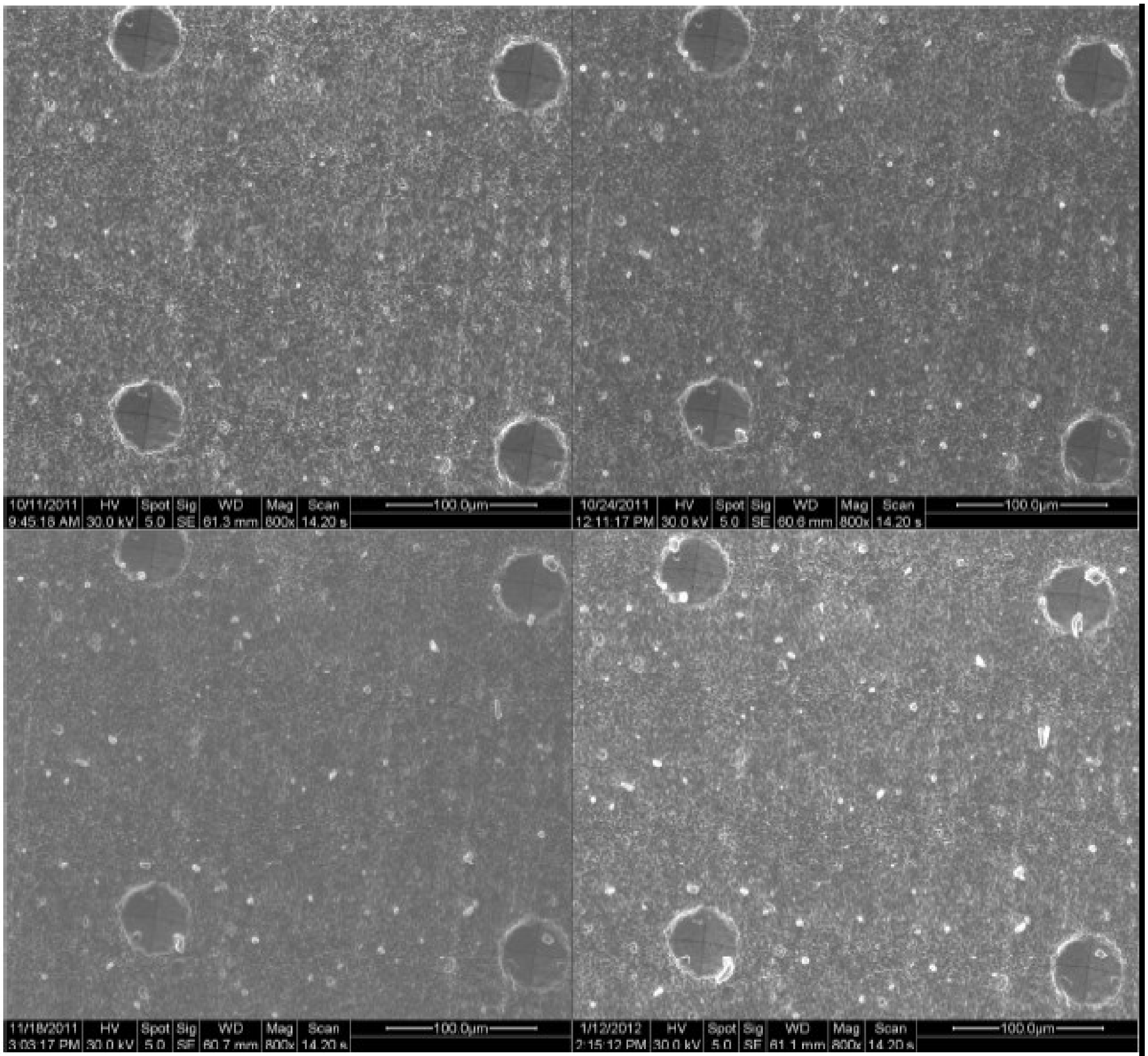

Figure 17 Whisker growth process on strongly elastically deformed sample. The sequence is a) 7 days; b) 20 days; c) 45 days, and d) 100 days post deposition.

The degree or amount of external stress provided through mechanical bending clearly influences whisker growth. Whisker growth is not a simple linear function of external bending stress applied. It appears that whiskers will increase in growth rate and number with increasing stress up to a certain critical stress, at which point whisker growth will then decrease. This critical stress point may be related to when the thin film plastically deforms and cracks form, thereby slowing whisker growth in a similar way as the cracks formed during gamma radiation.

Conclusions to Date

It has been demonstrated that digital image correlation and finite element method are viable tools to investigate the detailed deformation and stress states of the thin film system on a local level. Work performed to date is a calculation from the outside in, namely, given the deformation after the whisker has formed; the calculated results provide the post-growth state. By combining the finite element analysis at the microstructural level, such as modeling of the grain structures of tin and intermetallic compounds, more insight can be obtained.

Gamma irradiation testing appears to slow, if not prevent whisker formation. Additional effects of gamma radiation include crack initiation of the thin film, hillock growth, and nitrate formation. While the radiation exposure has proven to slow whisker growth, for military electronic system applications, the use of radiation may not be feasible.

Based on initial testing, the ratio of nitrogen/air in the gas environment surrounding the coated samples will influence whisker growth. Additionally, the degree of mechanical bending will influence whisker growth. The mechanism behind the driver for growth in both situations is unclear presently, therefore, further experimentation is needed regarding the mechanical bending of coated samples and the influence atmospheric composition on whisker growth as identified through the nitrogen/air mixture experimentation.