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

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Executive Summary

This report summarizes the research activities of WP-1754. The study focusses on the environmental factors influencing formation of lead free whiskers on electrodeposited tin coatings over copper (or copper containing) substrates. Much of the initial results are summarized in an interim report[i]. 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/nitrogen ratio in the formation of whiskers.

Different levels of elastic stress were induced with the incorporation of a custom designed fixture that loaded the substrates 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.

The effects of oxygen content were studied by aging substrates in gas vials of varying absolute pressure and different oxygen/nitrogen ratios. The concentration of whiskers were measured and appear to be sensitive to absolute pressure but are not sensitive to oxygen content (as previously observed)[i].

Introduction

Metallic whisker formation has been observed in lead free films of tin, cadmium and zinc since the 1940's[ii]. Increasingly, the use of lead free solder 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 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 environmentally induced phase changes. It is expected that this understanding will support the development of 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[iii]. Nucleation and growth of metallic whiskers has been proposed to be caused by the ingrowth of elastic stress in the tin film[iv]. Thermal cycles, coefficient of thermal expansion mismatch between the substrate and the surface film, density changes due to phase transformations, and the like, influence the stress state of the thin films and can, if extreme enough, lead to morphology changes such as whisker formation and growth. In the 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.

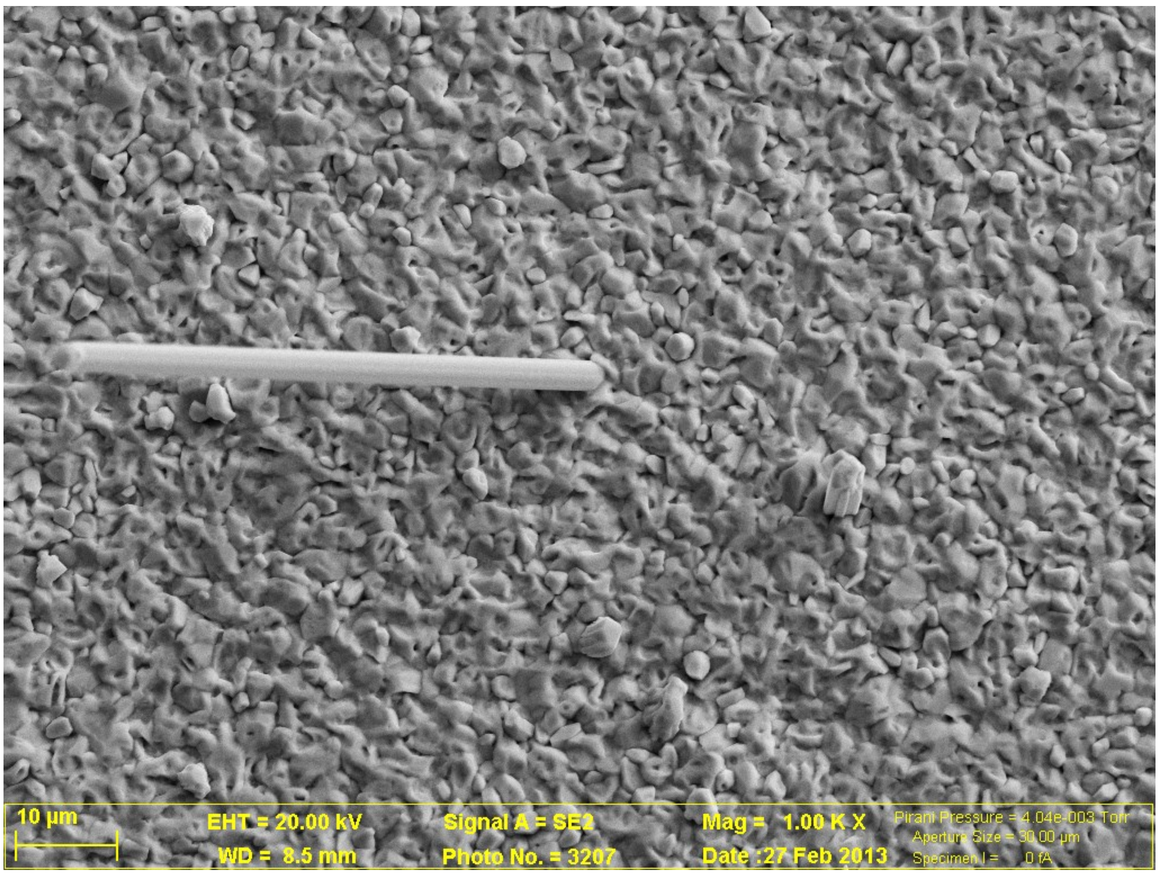


Figure 1: Secondary Electron Micrograph showing the surface of a tin film with whisker

The development of stress in thin films has been previously studied[iv]. 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[i]. With success, some areas of isolated compressive stress discontinuities were shown to occur when the substrate had external stresses applied to it. Four-point bend fixtures were fabricated be statically loaded to experimentally confirm this model.

Stress does not have to be externally induced. Phase transformation 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 the intermetallic forms stress level in the film increases (in higher compression) but not equally throughout. 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[i]. 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.

Methods

Sample Preparation: Samples were prepared at University of South Carolina (environmental tests) and Purdue University (bend tests). 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 constant current density, 4 mA/cm^2, was applied to reach a homogenous and continuous thin film. 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.

Samples for bend testing were prepared by electroplating tin films on substrates of copper and glass. Immediately before electroplating, the substrates were dipped in 98% sulphuric acid to remove the native copper oxide and then rinsed using ultrapure water. Copper substrates were electroplated with pure tin films to a thickness of 5µm using a commercial Sn plating solution. Electroplating was performed at a constant current density of 11mA/cm^2 using a cathode rotated at 200rpm.

Glass substrates were prepared by e-beam deposition of a 10nm Ti adhesion layer onto the glass, followed by a 300nm 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).

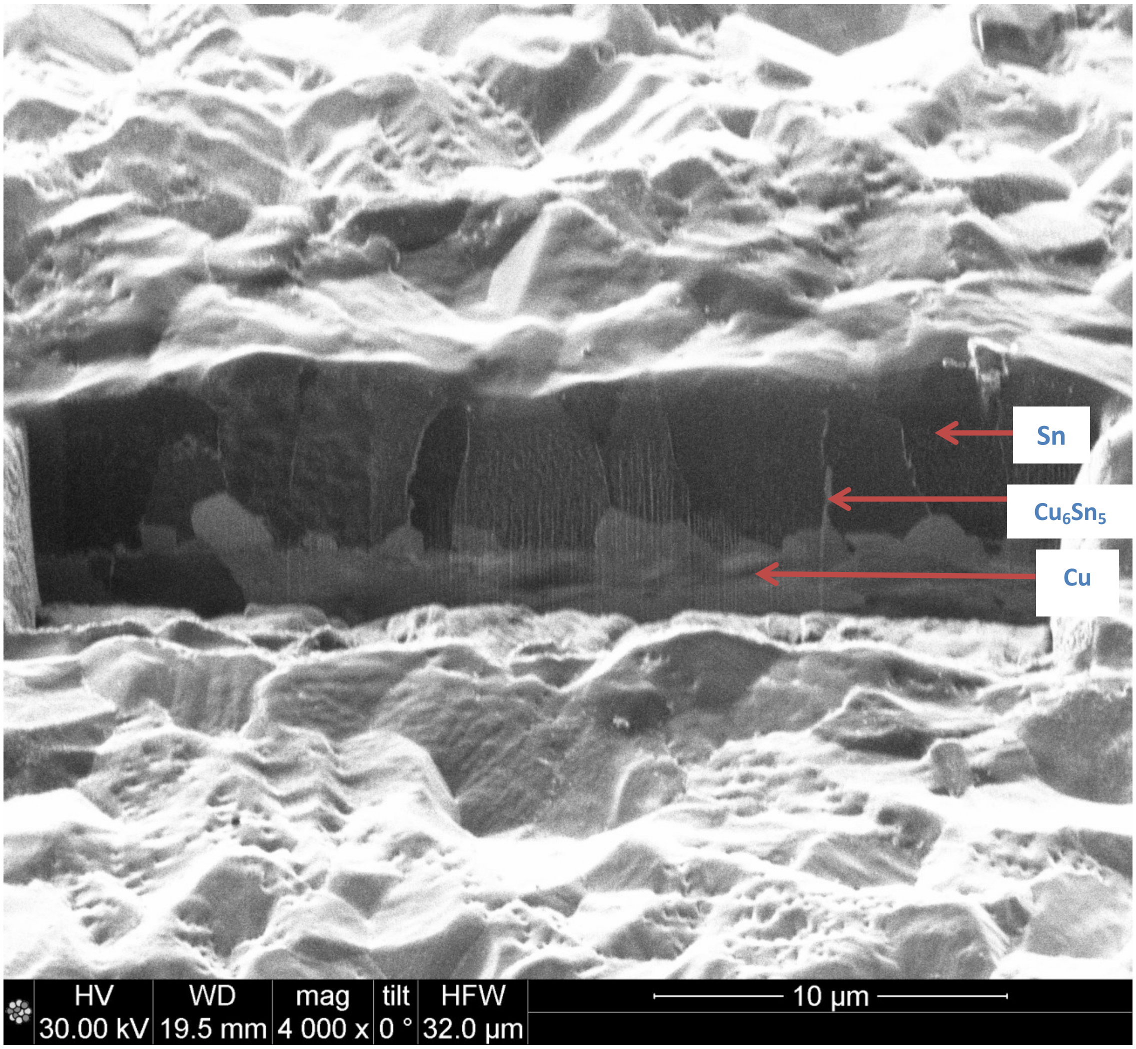


Figure 2: SEM Micrograph of Tin film on Copper Substrate cross-sectioned by FIB milling

Bend Tests: Four-point bend fixtures were configured to ASTM E 855 and C 1161[v, vi]. The bend fixtures (see Figure 3) were fabricated so sample could be statically loaded and held in an environmental chamber. 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 bimaterial strip model[vii] (see Figure 3), modifying the relation for the bending configuration. The required load was determined by the relation:

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

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)
$\mathbf{y_{max}}$ is the distance from the neutral axis to the top surface of the film = 0.304 mm (copper) and 0.503 mm (glass).

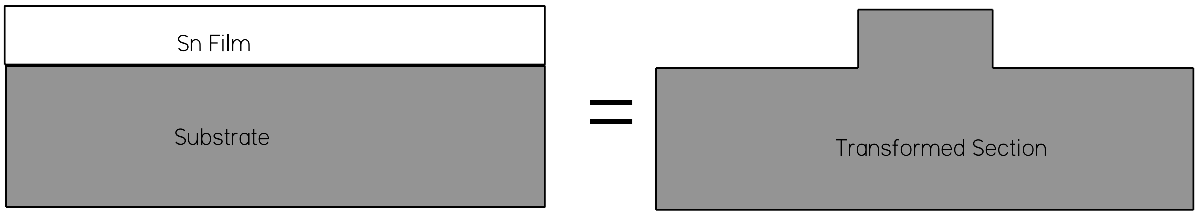


Figure 3: Transformed Section of bend specimen for bimaterial strip model (not to scale)

Pure tin films were grown of copper and glass substrates at Purdue University and loaded in the 4-pt. 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 matrix of samples was held for 720 hours and unloaded to characterize the amount of whisker formation. Discussions with the laboratory at Purdue led to a matrix of samples consisting of tin films on top of an evaporative coating of copper on glass substrates. The samples were held for approximately 600 hours and examined for whisker growth.

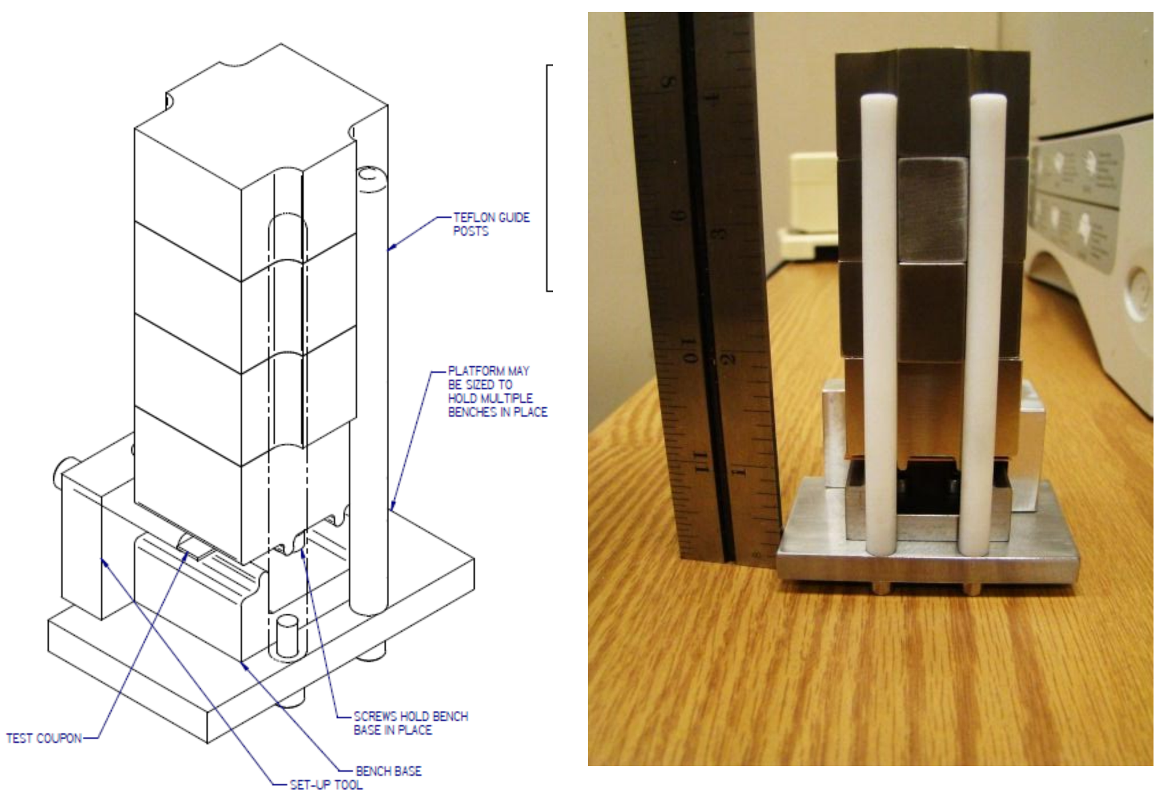


Figure 4: Four-point Bend Fixture Schematic a) and Assembled Configurations b)

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 in leak tight vessels. Gases were loaded into vessels at pressures of 0, 0.5, 1 and 4 atm (see Figure 4). 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 samples were discarded.

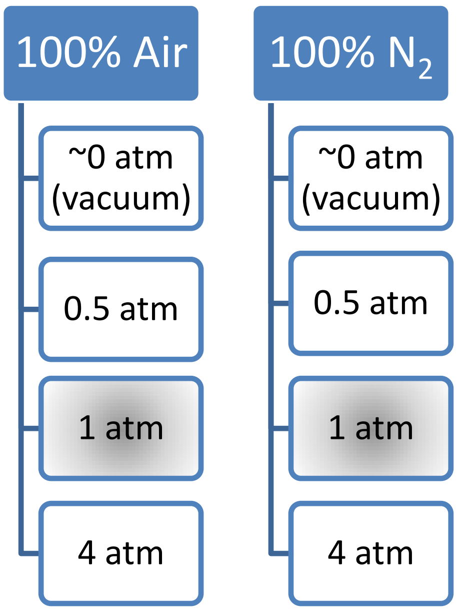


Figure 5: Matrix of Environmental Test Performed at Ambient Temperature

Characterization: Substrates were examined using scanning electron microscopy under secondary electron (SE) and backscattered electron modes (BSE). 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 # 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 6 and 7. 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 6, 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 ºC and 10% relative humidity for 720 hours. The results did not show substantial whisker growth on any of the samples. In Figure 7, the results from tin films on glass substrates 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 ºC 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.

Environmental effects on whisker formation in tin films were held for considerably longer than the bend test samples. Tin films grown on copper substrates were loaded in leak tight vessels and purged with gases at pressures of 0, 0.5, 1 and 4 atm. The vessels were held for a period of 200 days (4800 hours). The films were characterized and the results are summarized in Figures 7-11. 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. Both evacuated samples showed elevated whisker concentrations. In addition, when Figure 9-12 are studied it is evident that the whiskers that formed in the evacuated vessels exhibited high aspect ratios in comparison to the higher absolute pressures. The samples held at higher absolute pressure appear to grow more slowly.

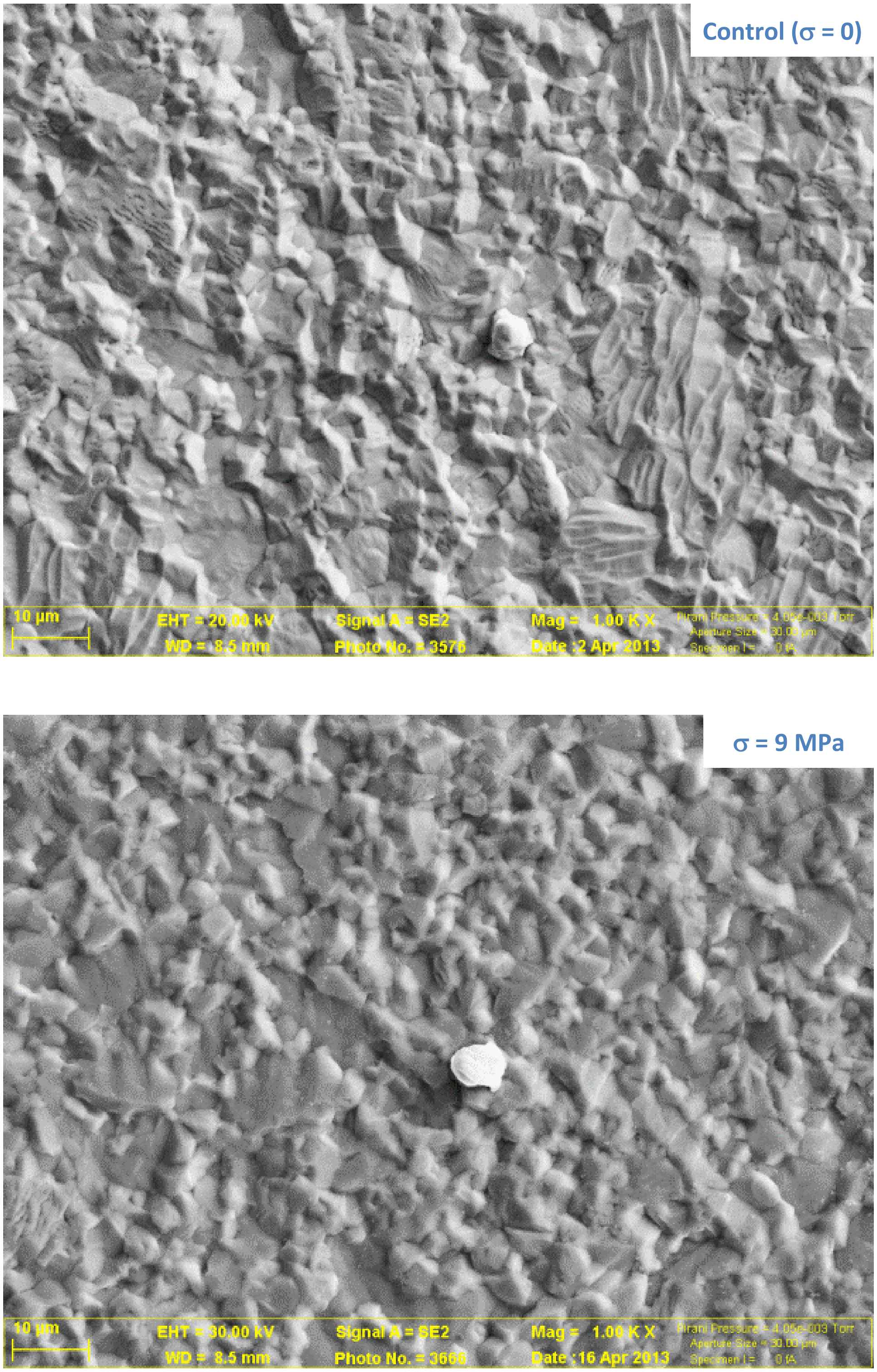
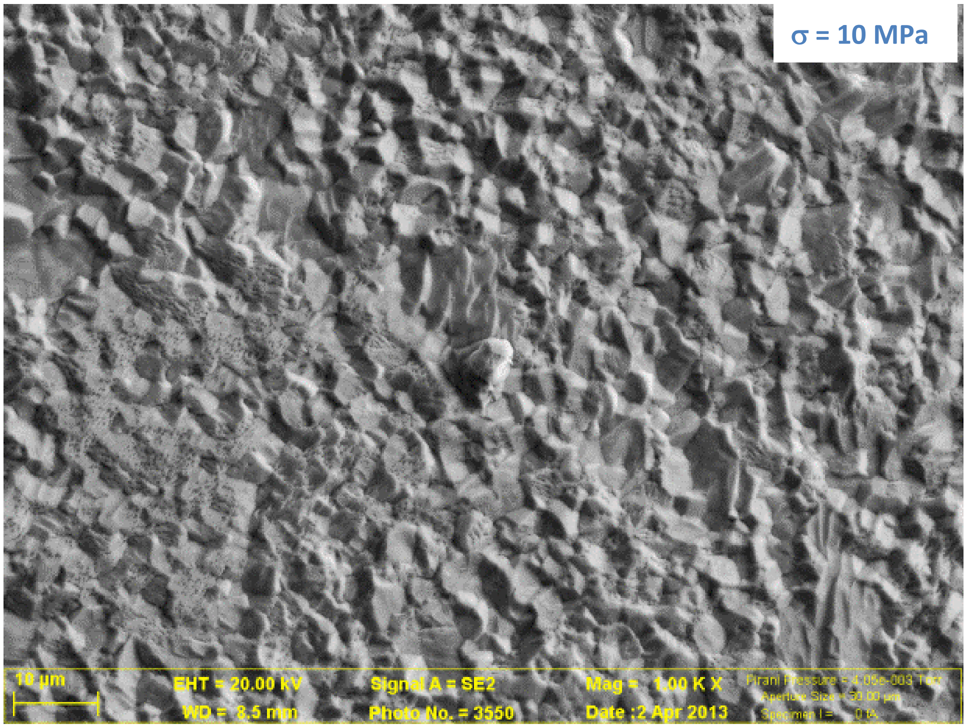


Figure 6: Four-point Bend Test Results of Sn film on Cu Substrates at Various Stress Levels after 760 hrs



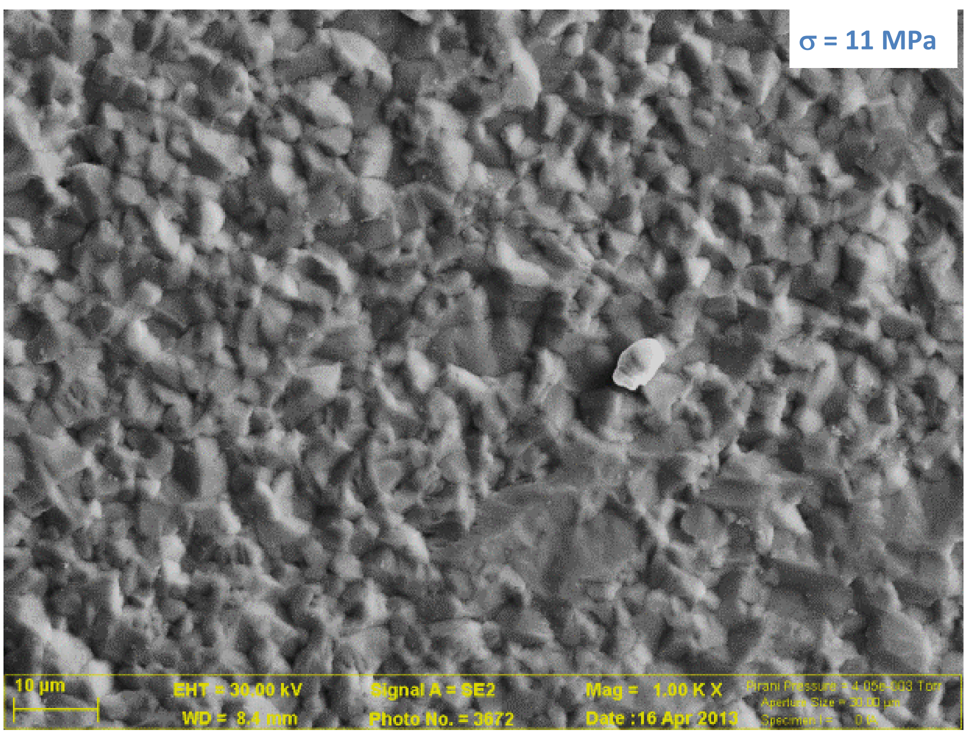


Figure 6 (continued): Four-point Bend Test Results of Sn film on Cu Substrates at Various Stress Levels after 760 hrs

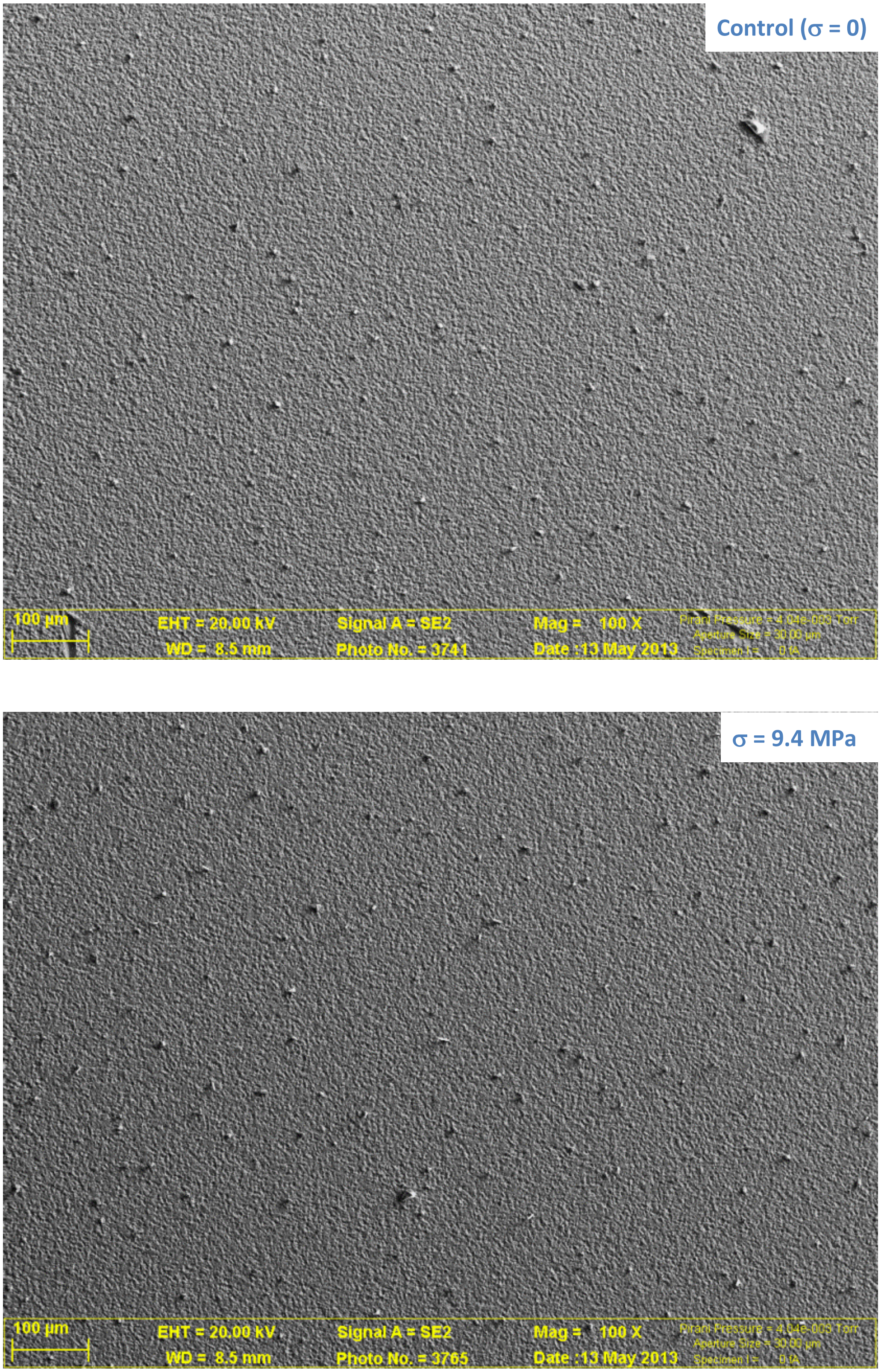


Figure 7: Four-point Bend Test Results of Sn film on Glass Substrates at Various Stress Levels after 600 hrs

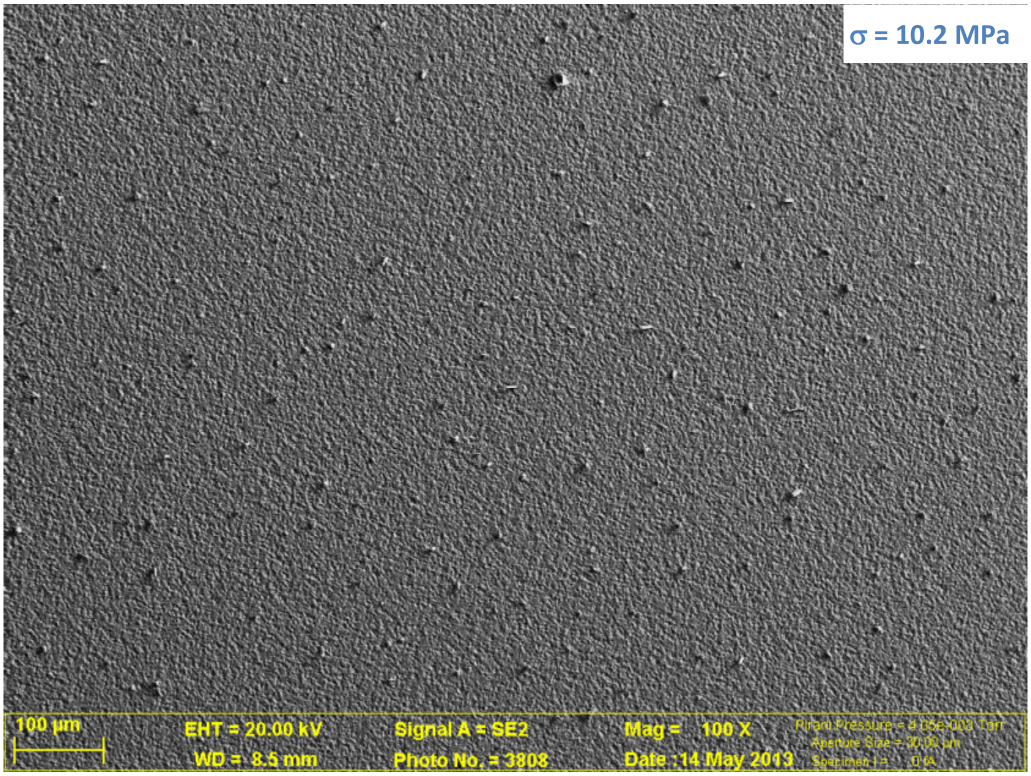


Figure 7 (continued): Four-point Bend Test Results of Sn film on Glass Substrates at Various Stress Levels after 600 hrs

Table 1: Concentration of Bend Tests of Sn film on 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

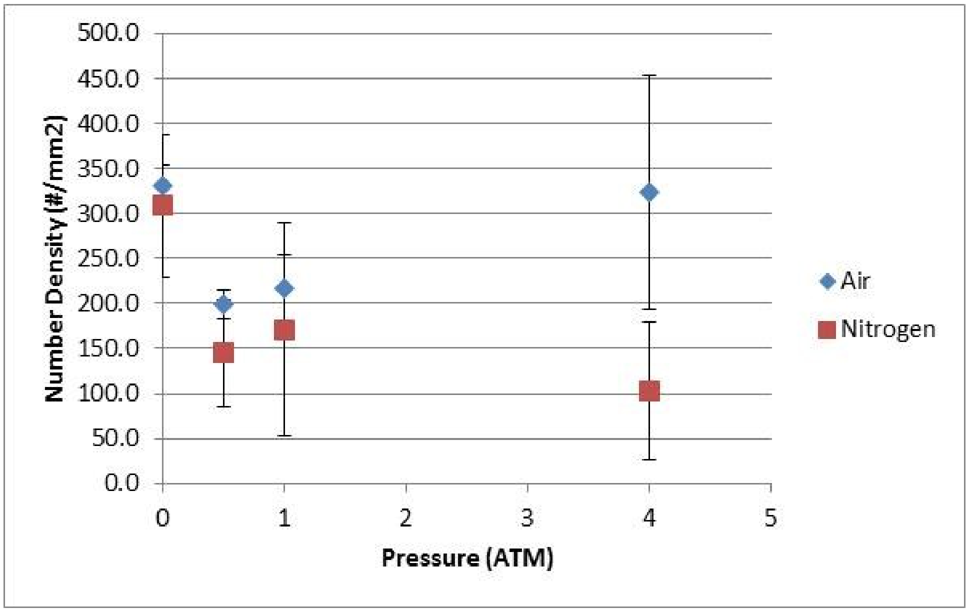
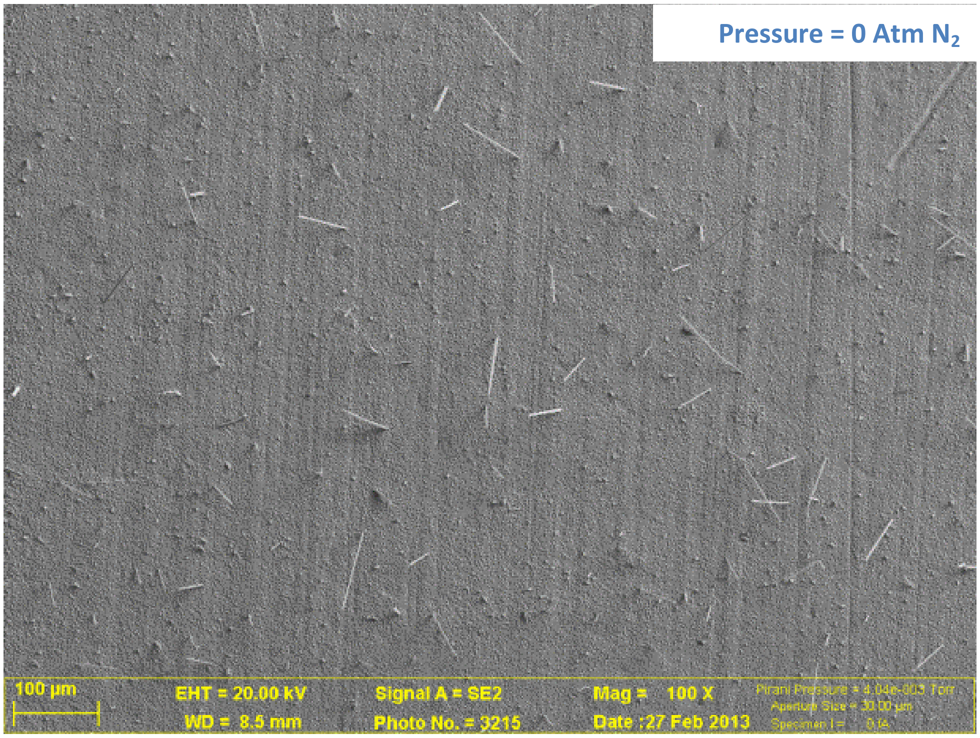


Figure 8: Number Density of Whisker/hillock appearance after ~200 days in the gaseous environment at various pressures



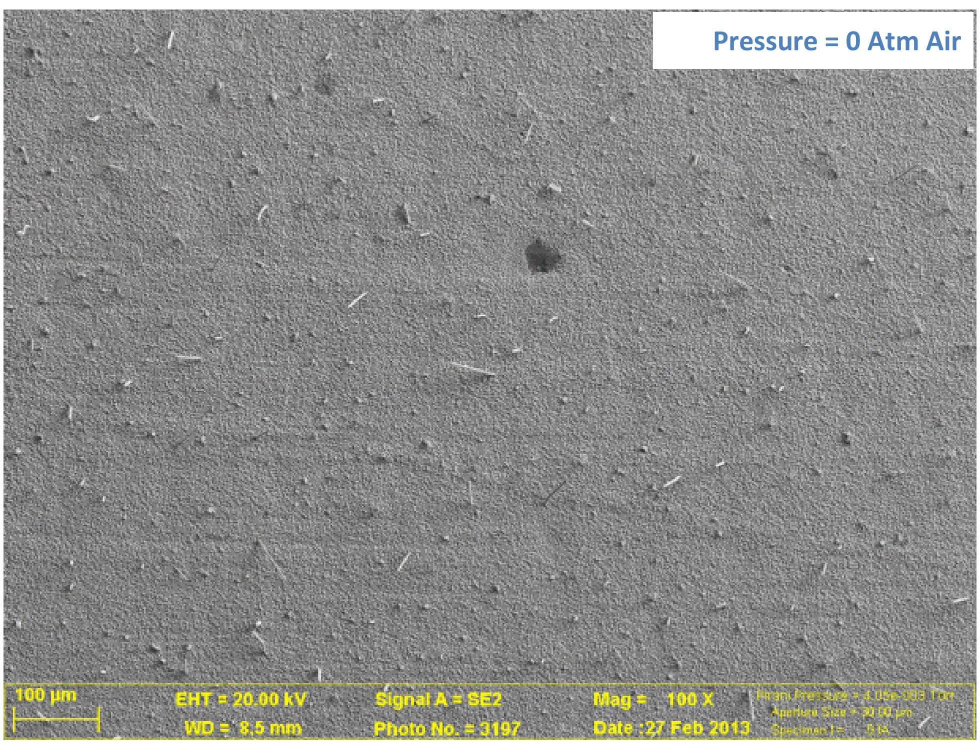
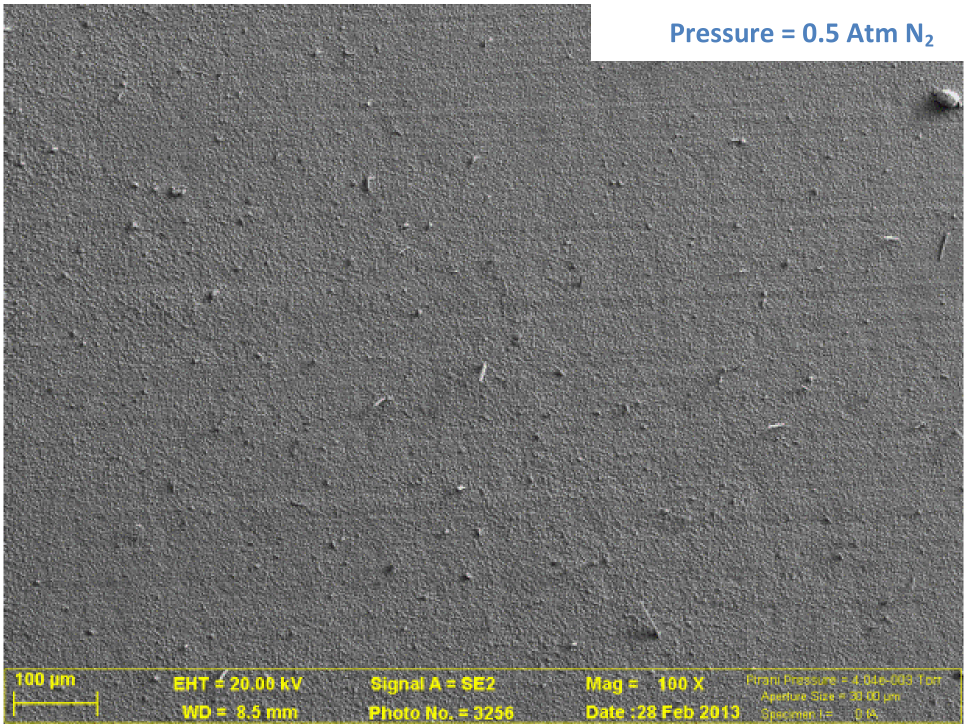


Figure 9: Environmental Testing of Sn film on Cu Substrates under Vacuum (0 atm) for 5200 Hours



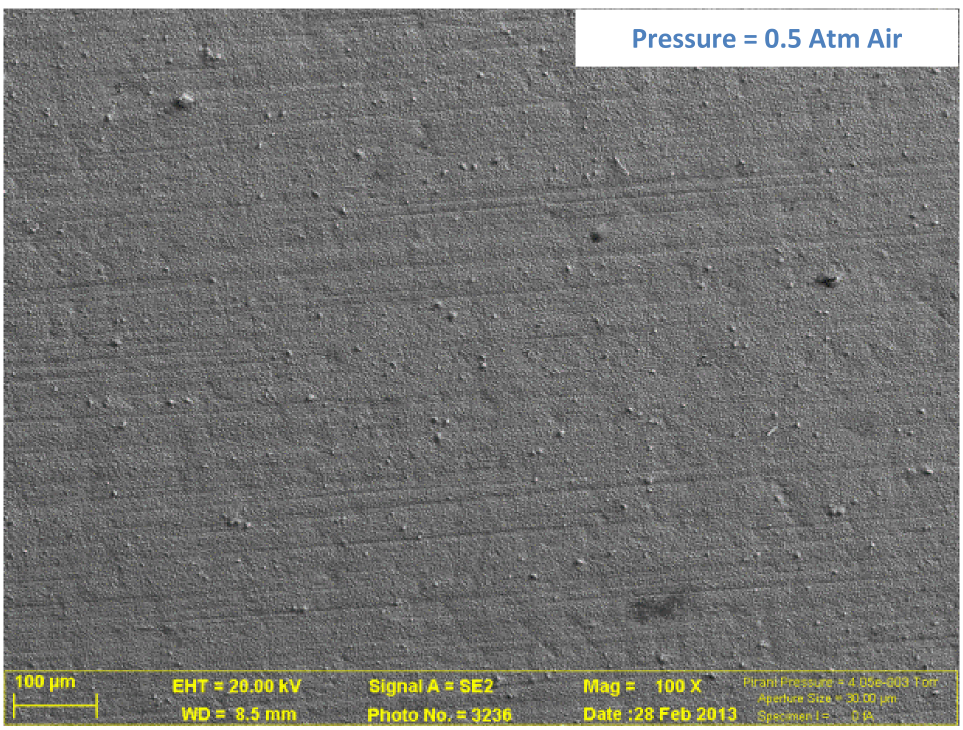


Figure 10: Environmental Testing of Sn film on Cu Substrates under 0.5 atm for 5200 Hours

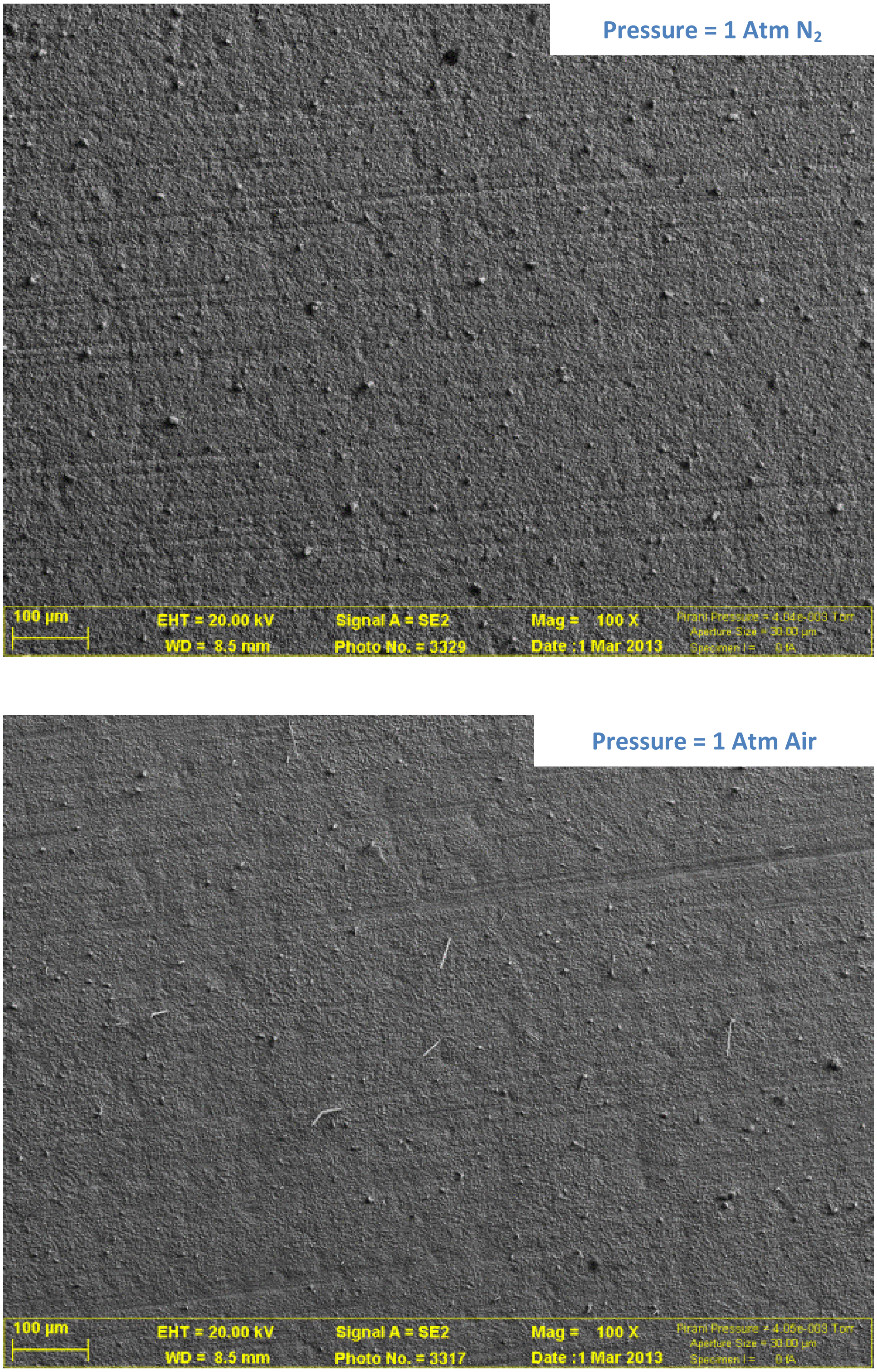
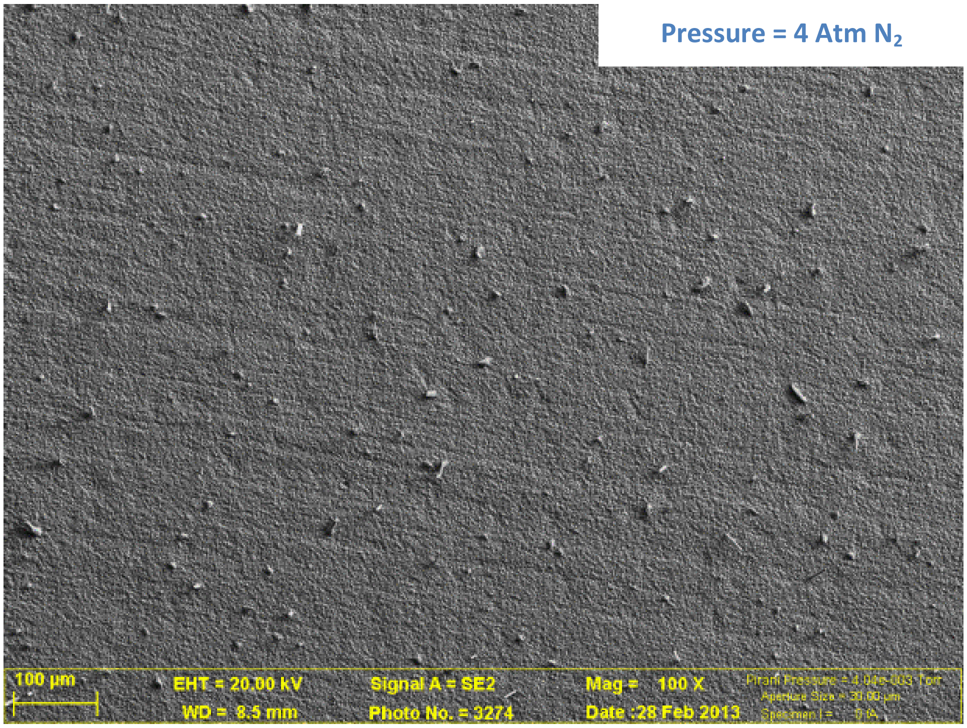


Figure 11: Environmental Testing of Sn film on Cu Substrates under 1 atm for 5200 Hours



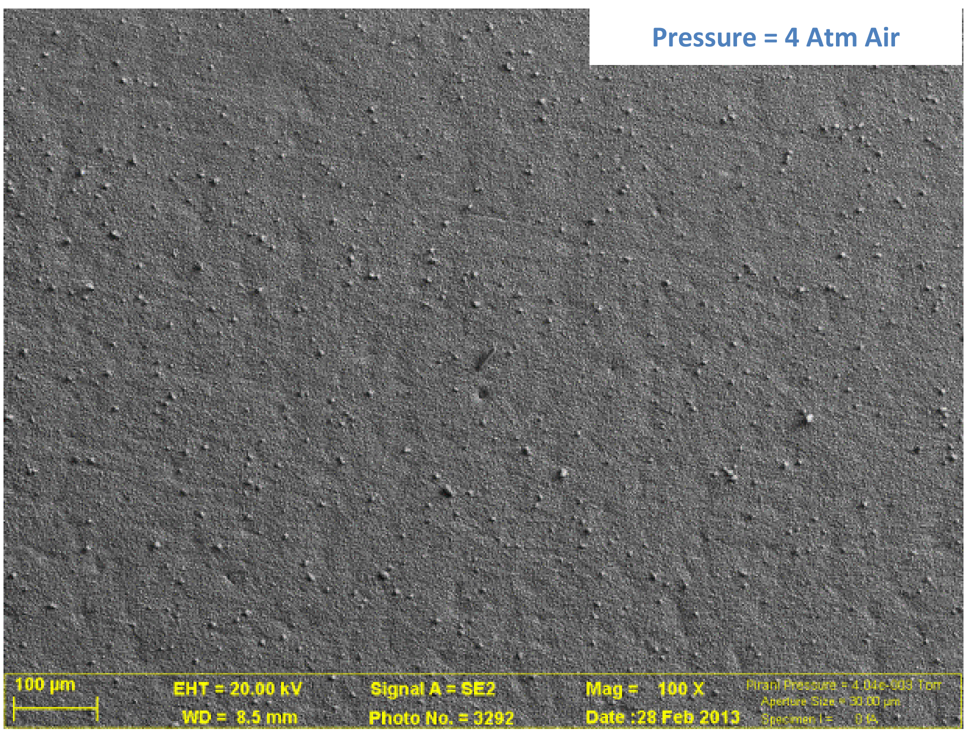


Figure 12: Environmental Testing of Sn film on Cu Substrates under 4 atm for 5200 Hours

Discussion

The results of the four-point bend tests did not yield a trend linking the degree of stress 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[iv]. The copper substrates exhibited slow rates of whisker formation at all levels of externally applied stress. The glass substrates tested exhibited more rapid rates of whisker formation. Although those samples that were loaded showed an increase in whisker density, this may not be statistically robust. 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 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 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/nitrogen ratio on whisker nucleation and growth. There is apparently not a statistically robust effect of oxygen/nitrogen ratio on whisker density and growth. However, lower absolute pressures did exhibit higher whisker densities of large aspect ratio whiskers. The role of oxide layers has been proposed to play a role in whisker growth[viii]. 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. The current study did not address the condition of the oxide layer prior to exposures in oxygen/nitrogen atmospheres and have not determined if the experimental atmosphere would cause a breakdown in the surface oxide. The stability of the oxide layer is vital to the understanding in order to discern the impact of oxygen/nitrogen ratios on whisker growth and is suggested for further study.

Conclusions

The environmental factors influencing formation of lead free whiskers on electrodeposited tin coatings over copper substrates was examined in the present study. The effects of elastic stress state on the nucleation and growth of whiskers was studied. The results show that induced elastic stress increased the concentration of whiskers, slightly. However, the statistical basis for this effect is insufficient to say conclusively.

The effects of oxygen content were also studied by aging substrates in gas vials of varying absolute pressure and different oxygen/nitrogen ratios. The concentration of whiskers/hillocks appears to be sensitive to absolute pressure but is less sensitive to oxygen content.

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