

Effect of Layer Properties on Stress Evolution, Intermetallic Volume, and Density during Tin Whisker Formation

Eric Chason, Nitin Jadhav, and Fei Pei

Compressive stress due to intermetallic (IMC) growth appears to be the main driving force for whisker formation, but many of the underlying mechanisms relating the IMC to stress and whisker formation are not understood. To better understand these fundamental processes, we have measured IMC, stress and whisker evolution in Sn layers deposited on Cu. We present systematic results of the effect of changing the Sn layer structure by modifying the grain size, thickness, Pb content, microstructure, and IMC morphology/growth kinetics. We have also made corresponding measurements of the mechanical properties of the Sn with similar changes in the structure and composition without the growth of IMC. We show that modifications that enhance the stress relaxation in the Sn also lead to reduced whisker growth.

INTRODUCTION

Tin whiskers are thin filaments (Figure 1) that grow out of Sn-based coatings used to protect conductors in electronics manufacturing. Sn whisker formation is an important reliability concern^{1,2} leading to failures in a number of high reliability systems such as satellites and missiles (as documented on the NASA website³). The problem has grown in severity with the advent of Pb-free manufacturing since the addition of Pb has been used since 1959⁴ to reduce the tendency to form whiskers.

The cross-section of the region around a whisker in Figure 2 reveals many of the important features that are believed to play a role in their formation. An intermetallic (IMC) layer is seen to form between the Sn and Cu layers, nucleating preferentially at the boundaries between Sn grains at the

Sn-Cu interface. As pointed out by Tu,⁵ the IMC grows preferentially into the Sn layer due to the greater diffusivity

of Cu in Sn versus the diffusivity of Sn in Cu. The Sn layer in this sample has a distinct columnar microstructure with an oxide layer covering the surface. In the image shown (Figure 2) the whiskering grain appears to extend all the way to the base of the Sn layer. In many cases, the whisker grain does not extend all the way into the Sn and has a horizontal grain boundary at its base with other Sn grains beneath it.⁶

It is believed by many that the driving force for the growth of whiskers is stress⁷ induced by the growth of the IMC within the Sn layer. However, there are many features of this that are not well understood, such as how the stress develops and how it leads to the formation of whiskers. In the current work, we present the results of experimental studies designed to illuminate aspects of the relationship among the IMC growth, stress and whisker evolution. In particular, we look at the effect of the Sn structure on the evolution of these parameters by changing the layer thickness, grain size and Pb-content and using heat treatments to modify the growth of the IMC layer. In so doing, we change the IMC growth rate and the stress relaxation processes in the Sn layer to observe their effect on whisker formation. We also present measurements of stress relaxation in different layer structures measured directly without the presence of Cu so that there is no IMC formation. Our results support the picture that the whisker growth is related to the stress and find that modifications that decrease the layer stress are correlated with a decrease in whisker growth.

RESULTS

In the following section, we present measurements for the evolution

How would you...

...describe the overall significance of this paper?

Sn whiskers that form on Cu conductors are a serious reliability risk in electronics manufacturing. Their presence has become a greater concern since the removal of Pb from Sn-based coating (Pb-free processing). In this work we measure the whisker formation on Sn coatings with different structures to relate the properties of the coating to the propensity to form whiskers. We show that coatings that have more stress in them due to intermetallic formation have higher whisker densities.

...describe this work to a materials science and engineering professional with no experience in your technical specialty?

Whiskers are believed to form on Sn coatings over Cu due to stress created by the growth of intermetallic at the Sn-Cu interface. Stress relaxation in the Sn can reduce the driving force for whisker formation. In this work we quantified the co-evolution of intermetallic volume, stress and whisker density on Sn layers with different properties (thickness, grain size, alloy composition, heat treatment). We find that enhancing the stress relaxation leads to fewer whiskers forming

...describe this work to a layperson?

Whiskers are thin filaments that grow out of tin coatings on copper surfaces and can cause short circuits. They have caused many documented failures, including the crashing of satellites. We are interested in understanding the processes that make them form so that we design structures that are less prone to whiskering. In this work we have investigated the effect of the tin structure on whisker formation to learn what features make them whisker less.

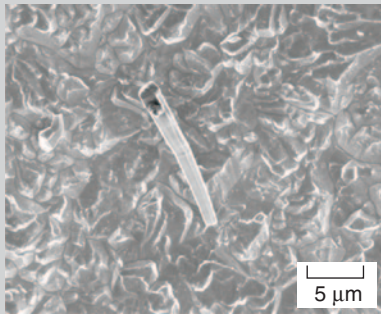


Figure 1. SEM micrograph of a Sn whisker growing from Sn surface.

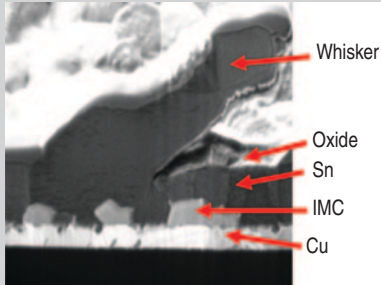


Figure 2. Cross section of a Sn layer plated over Cu. The arrows indicate the presence of whisker, oxide layer, Sn, IMC and Cu, respectively.

of IMC volume, Sn layer stress and whisker density growth, for a series of samples with different layer thickness, grain size, Pb content and annealing treatment. In the accompanying discussion we point out what these measurements tell us about the correlation among these measurements and the insight they give us into the mechanisms controlling whisker growth.

Samples with Different Layer Thickness and Grain Size

The first series of results were obtained from samples of pure Sn on Cu with different thickness as shown in Figure 3. The sample structures are also shown schematically in Figure 3a–c. The SEM image below the schematic (Figure 3d–f) shows the surface after the Sn has been etched away revealing the formation of IMC at the Cu/Sn interface. Because the IMC (white dots on the picture) grows preferentially at the Sn grain boundaries, its structure reveals the grain size that the Sn layer had before it was etched away. As seen in previous work,^{8,9,16} the grain size increases with the layer thickness.

The co-evolution of IMC, stress and whisker density made on a series of samples is shown in Figure 3g–o). The solid symbols for the IMC and stress represent measurements made on

EXPERIMENTAL BACKGROUND

The Sn-based layers were grown by electrodeposition using commercial plating solutions for pure Sn and Pb-Sn compositions. For the whisker growth studies, the Sn-based layers were grown over Cu layers that were vapor deposited via electron-beam deposition on oxidized Si (100) substrates. For the samples used for the stress relaxation measurements, a thin 0.5 micron Sn layer was vapor-deposited before the subsequent electrodeposition of the thicker Sn or Pb-Sn layer. In both cases, a 15 nm Ti interlayer was electron-beam deposited initially to enhance adhesion. Further details of the sample preparation can be found in References 8–10.

To measure the evolution of the IMC volume and stress, a number of samples were made at the same time with identical structures and then measured at different time intervals after preparation. The IMC volume was determined using a weighing technique that had been developed previously.^{8,11,12} This is done by weighing each sample after the Cu layer is deposited and again after the Sn layer is deposited so that the mass of deposited Sn in each sample can be determined. After the desired time interval, the sample is etched using a solution that selectively removes the Sn layer without affecting the IMC or underlying Cu. The difference in weight between the deposited layer and the amount removed by etching corresponds to the weight of Sn that has been incorporated into the Cu₆Sn₅ IMC. The morphology of the IMC at the Cu-Sn interface can also be measured using SEM on the sample surface after the Sn layer was removed. The same method was used for Pb-Sn alloy samples with same etching solution.

The evolution of the stress in the Sn layer was monitored using an optical wafer curvature technique (MOSS)¹³ on the same samples used to determine the IMC volume. In this technique, the curvature (1/R) is obtained by measuring the deflection of an array of parallel laser beams reflected from the sample surface relative to a flat surface. The curvature of the substrate can then be related directly to the stress in the film using Stoney's relation.¹⁴ For a multilayer structure such as in these experiments, the curvature is approximately given by the following sum over the average stress in each layer multiplied by the layer thickness:

$$\frac{1}{R} = \frac{6}{M_s h_s^2} [\langle \sigma_{Cu} \rangle h_{Cu} + \langle \sigma_{IMC} \rangle h_{IMC} + \langle \sigma_{Sn} \rangle h_{Sn}] \quad (1)$$

where $\langle \sigma_i \rangle$ is the average stress and h_i is the thickness of each layer of the film (Cu, IMC, and Sn). M_s and h_s refer to the biaxial modulus and thickness of the substrate, respectively. The average stress is defined in terms of an integral of the in-plane stress over the thickness of the layer. Although the layers may not be homogeneous and uniform, we have approximated the actual stress by its average value for an equivalent layer of uniform thickness.

To determine the evolution of the stress with time, we measured the curvature in the same samples that were used for determining the IMC volume. As shown by Equation 1, the curvature is due to multiple layers so that the stress in the individual layers cannot be determined from a single measurement. To determine the stress in the Sn alone, we therefore measured the curvature again after the Sn layer was removed by the selective etch. The difference in the curvature between the full sample and the sample with the Sn layer can then be attributed to the product of $\langle \sigma_{Sn} \rangle h_{Sn}$ for the Sn layer alone. Note that the thickness of the Sn layer is also obtained directly from the weighing measurement.

An additional sample was monitored continuously in real-time to determine the density of whiskers and hillocks on the surface. This is accomplished using an optical technique that monitors the scattering of light from the surface¹⁵ in a manner similar to the monitoring of particle defects on Si wafers. By using oblique illumination in an optical microscope, we can count the density of surface features over a large area even though they are too small to be individually resolved. This enables the surface to be monitored non-destructively over long periods of time with a simple optical system that can be easily quantified. Note that it does not measure the size or shape of the features, only the density.

samples that were all fabricated at the same time and then measured at different time intervals. The non-destructive whisker density measurement (Figure 3m–o) was performed continuously over the same period on a single sample.

A similar trend is seen in all the data. The IMC layer grows continuously

with a rate that decreases over time. It eventually exhibits a square root of time behavior,¹⁷ presumably limited by diffusion of Cu across the IMC layer that forms at the interface. The corresponding stress in the Sn layer initially exhibits a rapid change from an as-deposited tensile film to a compress-

Table I. Measured Grain Size in Sn Layers of Different Thicknesses

Sn Layer Thickness (nm)	Grain Size (μm)
1,450	1.42
2,900	1.92
5,800	3.22

strates without the presence of IMC.⁹ In these experiments, the stress is induced by heating the sample due to the thermal expansion mismatch between the Sn and Si and is monitored using wafer curvature. The measured stress vs. temperature is shown in Figure 4 for both a thin (1.5 micron) and thick (8 micron) Sn layer. The sample was heated at a constant rate and then held at the highest temperature for 5 hours before being cooled to room temperature. The deviation from linearity during the heating cycle is due to the onset of plastic deformation in the layer. The thick layer has significantly greater relaxation than the thin layer, which is consistent with the lower steady state stress observed for the Sn layers on Cu. The exact mechanism for the enhanced relaxation is not understood, but similar results are found in many studies^{19,20} that indicate stress relaxation is suppressed in layers with small grain size.

The density of whiskers is found to be lowest in the thickest layers. These layers also have the lowest stress levels, so this result is consistent with the reduction in stress leading to a reduced whisker growth rate. However, because the grain size is also different, the result may also be due to the different microstructure of the layer. To resolve this ambiguity, in the following section we describe measurements on Sn layers which had the same grain structure but different thickness.

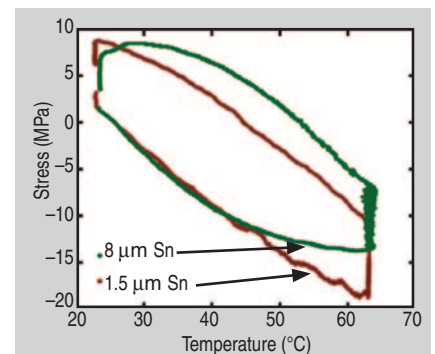


Figure 4. Stress versus temperature during thermal cycling from 23°C to 63°C for 1.5 μm and 8 μm Sn layers.

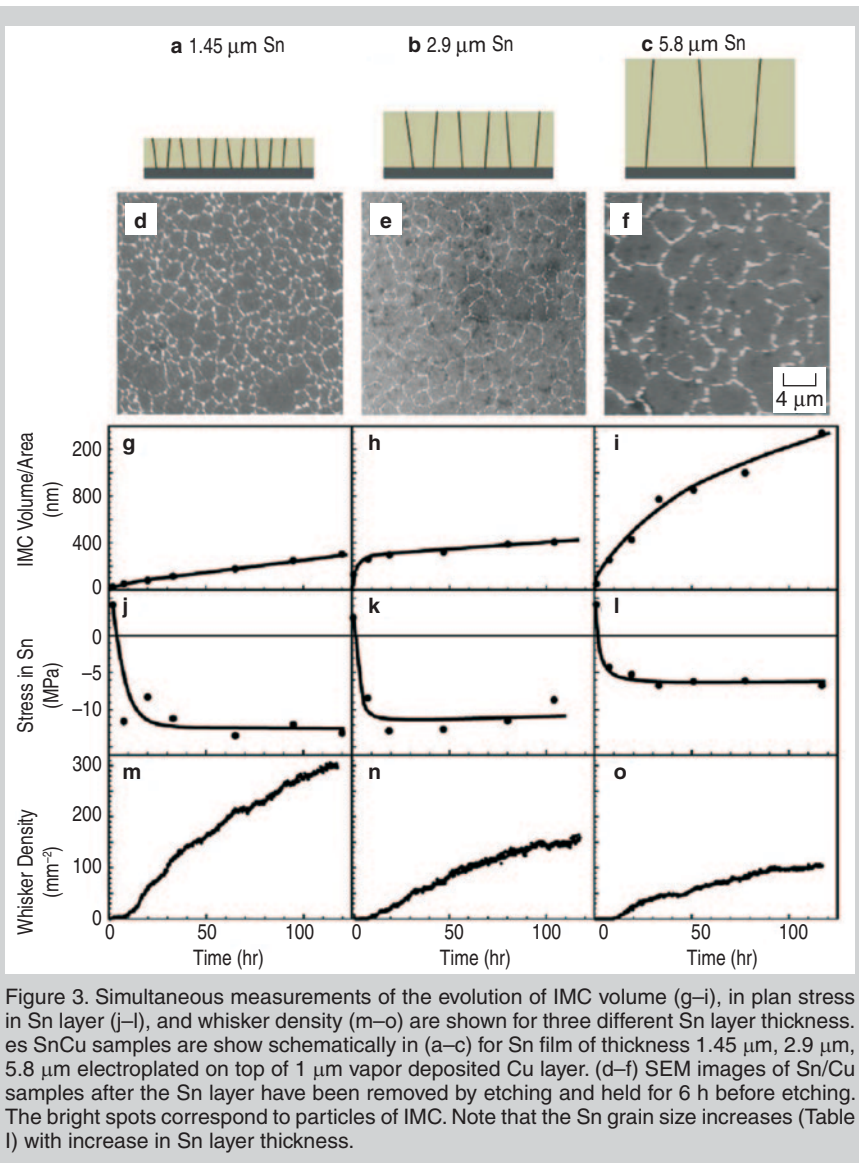


Figure 3. Simultaneous measurements of the evolution of IMC volume (g–i), in plan stress in Sn layer (j–l), and whisker density (m–o) are shown for three different Sn layer thicknesses. SnCu samples are shown schematically in (a–c) for Sn film of thickness 1.45 μm , 2.9 μm , 5.8 μm electroplated on top of 1 μm vapor deposited Cu layer. (d–f) SEM images of Sn/Cu samples after the Sn layer have been removed by etching and held for 6 h before etching. The bright spots correspond to particles of IMC. Note that the Sn grain size increases (Table I) with increase in Sn layer thickness.

sive state. Although the IMC layer continues to grow, the stress saturates at a steady-state value. In previous work,¹⁸ we have shown that this stress evolution can be explained in terms of a balance between stress generated by the expansion of the IMC into the Sn layer and relaxation by a combination of plasticity and creep mediated by diffusion along the network of grain boundaries. The whisker density increases with time but only after an incubation period that corresponds roughly to the time it takes for the stress to reach its steady state compressive value.

Comparison of the evolution curves for different layer thicknesses sheds light on the underlying mechanisms controlling the whisker formation. IMC growth is seen to be much more rapid in the layer with larger thickness (Figure 3m) than the thinner layer

(Fig 3o). This is most likely due to the larger grain size in the thicker layer (Table I), since the IMC growth occurs at the Sn/Cu interface and would therefore not be expected to depend on the thickness of the layer. The increase of growth rate with grain size indicates that the growth rate may be controlled by diffusion of Cu in the intragranular region of the Sn layer where the IMC forms more slowly than at the Sn grain boundaries.

Interestingly, even though the thicker/large-grained layer has more IMC growth, we find that the steady state stress is less in this structure than in the thinner layer. This suggests that the stress relaxation processes are more rapid for thicker/large-grained Sn layers. To investigate this further, we measured the stress relaxation behavior directly in Sn layers grown on Si sub-

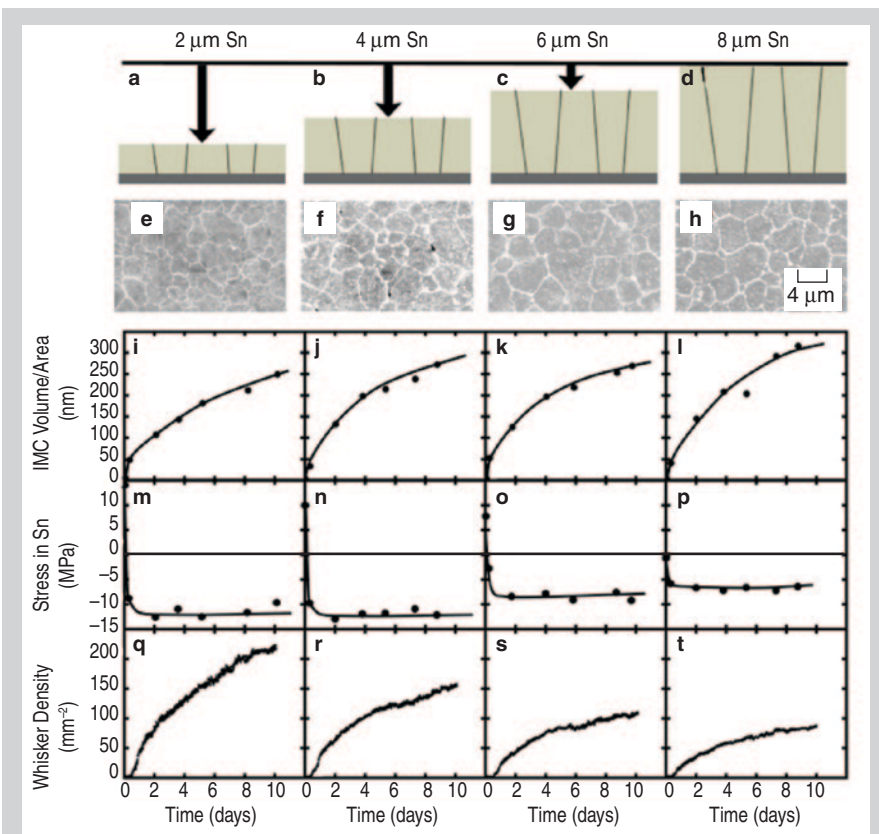


Figure 5. Influence of Sn layer thickness when grain size remains constant. An 8 μm Sn film was electroplated on all specimens. The samples were then partially etched to leave Sn layers of difference thickness on the 1 μm vapor deposited Cu layer. The process is shown schematically in (a–d). SEM micrographs (e–h) of the Sn/Cu interface obtained by selectively etching Sn layer indicate that the grain size (Table II) is comparable for all. Simultaneous measurement of IMC volume (i–l), Sn stress (m–p), and whisker density (q–t) for different Sn thickness.

Samples with Different Thickness but Same Grain Size

To separate the effects of grain size and layer thickness on whisker growth, we prepared a series of samples that had different layer thickness but the same lateral grain size. As discussed in the previous section, increasing the layer thickness tends to increase the grain size. Therefore, to keep a constant grain size, we used the process shown schematically in Figure 5. These samples were created by first growing the layer to a thickness of 8 microns and then etching it back to the desired thickness. The sample structures are shown schematically in Figure 5a–d.

Table II. Measured Grain Size in Sn Layers That Were Etched from 8 μm to Different Thicknesses

Sn Layer Thickness (μm)	Grain Size (μm)
2	3.92
4	4.03
6	4.28
8	3.94

The corresponding SEM images of IMC growth as shown in Figure 5e–h shows that this resulted in layers of different thickness but the same nominal grain size.

The evolution of the IMC volume, stress and whisker density for this series of samples is shown in Figure 5i–t. The layer thickness is indicated at the top of the figure. In this case, the growth rate of the IMC does not depend strongly on the layer thickness, in contrast with the results discussed previously. This confirms that the IMC growth rate is greater for larger grain size but does not depend on the thickness of the layer. We also find that the steady state stress depends on the layer thickness even when the grain size is kept constant (Table II). The steady-state compressive stress is lower for the thicker layers, suggesting that relaxation is enhanced by increasing the length in the vertical direction (layer thickness) as well as in the horizontal direction (grain size).

Most importantly, we find that the

whisker density is lower for layers with greater thickness. In this case, the grain structure (i.e., texture, lateral grain size) is the same for all the layers thicknesses so it cannot be attributed to a change in the microstructure. Therefore, this appears to confirm that the density of whiskers that forms depends on the amount of stress in the layer.

Effect of Lead Alloy Addition on Whiskering

It is well known that the addition of Pb to Sn-based coatings significantly suppresses the tendency to form whiskers⁴ which is why the advent of Pb-free manufacturing has led to a resurgence in the problem. To understand how Pb reduces whisker formation, we measured the evolution of IMC, stress and whiskers on Pb-Sn alloy layers for comparison with the pure Sn. The layers have the same thickness and the grain size of the Pb-Sn layer is comparable to the grain size in the pure Sn layer.

The results, shown in Figure 6, provide insight into how Pb modifies the properties of the Sn layer. With respect to the IMC growth rate (Figure 6a), we find that the addition of Pb does not significantly change the rate at which it forms. This is not necessarily surprising since IMC formation is needed in order to form a good solder joint and Pb-Sn alloys make good solders. However, it does show that Pb does not prevent whiskers by shutting down the IMC growth rate.

The major effect of Pb addition is seen in the evolution of the stress (Figure 6b). For the same amount of IMC as that formed in pure Sn, the stress in the Pb-Sn layers is significantly reduced relative to pure Sn. Consequently, the density of whiskers formed over the same period is essentially zero, much less than the case for the pure Sn sample of the same thickness (Figure 6c).

The small amount of stress observed in the Pb-Sn layers on Cu suggests that the addition of Pb greatly enhances the rate of stress relaxation. We therefore performed direct measurements of stress relaxation in Pb-Sn alloy layers to determine if this is indeed the case. Results of stress measurements during thermal cycling are shown in Figure 7

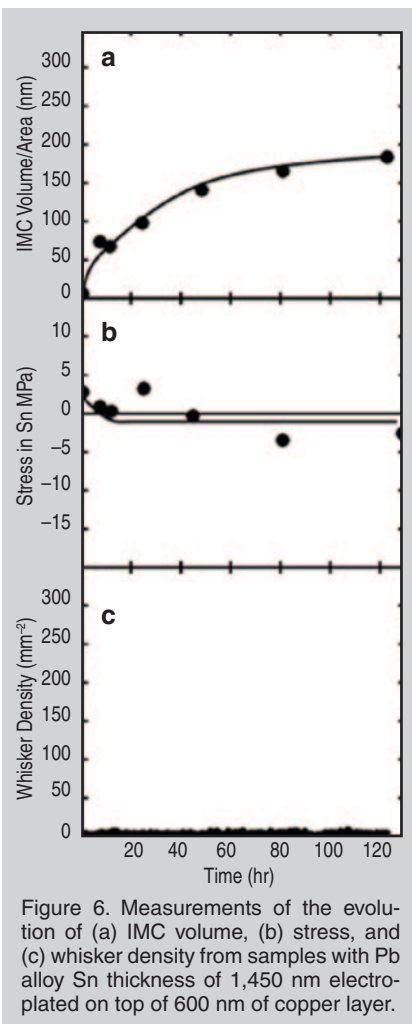


Figure 6. Measurements of the evolution of (a) IMC volume, (b) stress, and (c) whisker density from samples with Pb alloy Sn thickness of 1,450 nm electroplated on top of 600 nm of copper layer.

for 8 micron thick layers of Sn and Pb-Sn. For the same temperature increase, the amount of stress is clearly reduced in the alloy layer relative to the pure Sn.

The reason for the enhanced stress relaxation in Pb-Sn has been attributed to the different microstructure for the different compositions. As pointed out by Boettinger et al.,²¹ the addition of Pb changes the structure from columnar to one that is more equiaxed as seen by comparison of the cross sectional FIB/SEM images for a pure Sn and a Pb-Sn layer (shown in Figure 8). Boettinger et al. and others⁶ have suggested that the presence of horizontal grain boundaries in the alloy layers provide sinks for diffusing atoms to go to which accommodates the strain induced by the IMC growth without creating stress in the layer. To address this issue, we have also made stress-relaxation measurements of 1 micron thick Pb-Sn layers on Si.⁹ In this case, the layers are not thick enough to form horizontal grain boundaries so that the microstructure

remains columnar. In this case, we find that the stress relaxation is not enhanced even though the layer contains Pb. This strongly suggests that the presence of the horizontal grain boundaries is the reason that the stress relaxation is increased. In other work, Yu²² has shown that a non-columnar Sn structure is also sufficient to suppress whisker formation.

Effect of Heat Treatments (Annealing and Reflow)

In addition to alloying with Pb, heat treatments are another common means of delaying whisker formation. For this work, we wanted to study a system similar to that used in industry, so Sn layers of 10 μm thickness were electroplated over a 1 μm vapor deposited Cu layer on Si substrates. Four pairs of samples were prepared at the same time and subjected to different heat treatments. Annealing (holding the sample for 60 min. at 150°C) and reflow (heating the sample to 150°C and holding, followed by heating to 225°C) are shown schematically in Figure 9. Another two samples were annealed followed by reflowing and two samples were monitored without any heat treatment. The annealing was performed within 30 min. of the Sn deposition and reflowing was done with 24 h of Sn electroplating.

Because the annealing treatments lengthened the time for whiskers to form, these samples were monitored over a much longer period than in the studies described above. One sample of each type was used to measure the IMC volume and stress at a time of 13 days after the Sn deposition. The other sample was monitored for whisker density over a period of 100 days and then etched after 145 days to measure IMC formed and stress in Sn layer.

The amount of IMC measured at each time for the different anneal-

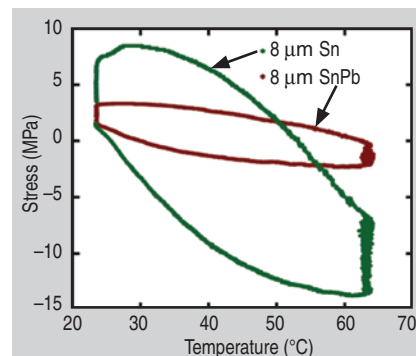


Figure 7. Stress versus temperature during thermal cycling from room temperature (23°C) to 63°C for an 8 μm Sn layer and 8 μm Pb-Sn alloy layer.

ing sequences is shown in Figure 10. All the samples that were heat treated had more IMC than the sample kept at room temperature by a factor of 4–5. For these samples, a large part of the IMC most likely formed during the heat treatment since the change in volume between day 13 and 145 was much less than the initial volume measured.

Figure 11 shows the Sn-Cu interface observed in the SEM after etching away the Sn layer for the 13 day measurement. All the heat-treated samples have a more uniform and thick IMC than the untreated sample. EDX analysis showed that the layer composition was roughly 78% of Cu and 22% of Sn, indicating that the IMC phase that formed was Cu_3Sn , which is more stable compared to Cu_6Sn_5 at high temperature. This also indicates that the IMC formed while the sample was held at elevated temperature. In comparison, EDX of the room-temperature sample showed that the composition is consistent with the Cu_6Sn_5 phase. The greater thickness and uniform morphology of this IMC presumably impedes Cu diffusion and therefore slows further IMC formation. In comparison, the sample which was kept at room temperature had a smaller amount of intermetallic that formed preferentially at the Sn grain boundary. The discontinuous

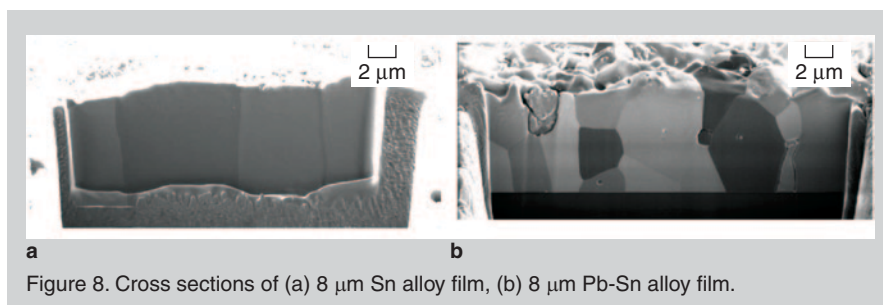


Figure 8. Cross sections of (a) 8 μm Sn alloy film, (b) 8 μm Pb-Sn alloy film.

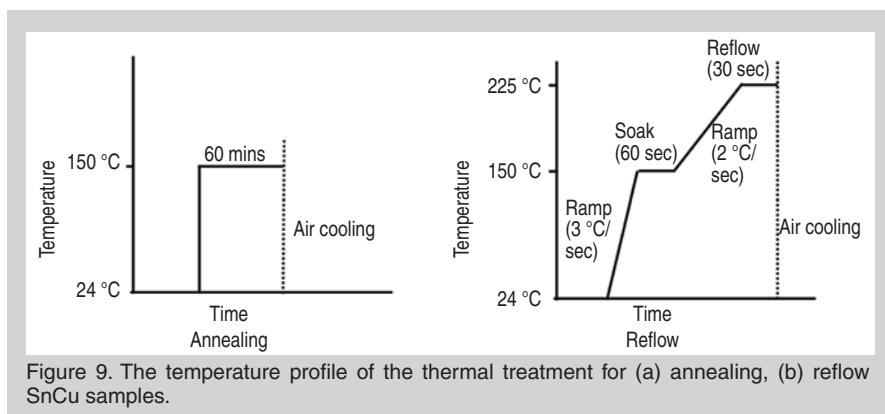


Figure 9. The temperature profile of the thermal treatment for (a) annealing, (b) reflow SnCu samples.

non-uniform nature of this layer nature allowed the IMC to continue to grow, though the total change in IMC volume between day 13 and day 145 is not much greater than for the other samples (and perhaps less than for the annealed sample).

The corresponding stress in the layers is shown in Figure 10b measured after the 13th and 145th days. The effect of the heat treatment on the stress state is dramatic. In comparison with the compressively-stressed room temperature samples, all the heat-treated samples are in a tensile stress state. This is true even though there has been a significant amount of IMC formed in the layer. The reason for the tensile stress is the thermal mismatch strain between the Sn layer and the Si substrate that develops during the annealing/reflow processes. As shown in the heating cycles used for measuring stress relaxation (in Figure 9), the Sn layer develops a tensile stress after it has been held at elevated temperature and then cooled to room temperature. Since this occurs after the bulk of the IMC is grown, the layer remains in a state of tensile stress.

In the corresponding whisker density is shown in Figure 12, clearly each of the heat-treatments has effectively suppressed whisker formation relative to the sample held at room temperature. We attribute the whisker reduction to the fact that the Sn layer in all the heat treated samples had tensile stress.

SUMMARY AND IMPLICATIONS FOR WHISKER MITIGATION

We have studied the co-evolution of IMC volume, stress and whisker density in Sn-based layers on Cu in which we systematically varied the thickness,

grain size, Pb content and thermal treatment. The results enable us to make the following conclusions about the relationship between these parameters. The rate of IMC growth increased with the grain size but was not dependent on the thickness of the layer for constant grain size. This is consistent with the observation that the IMC grows out from the Sn-Cu interface and therefore should not depend on the thickness. Similar amounts of IMC formed in Pb-Sn alloys and pure Sn, indicating that alloying with Pb doesn't stop the IMC formation

The stress in the Sn layer rapidly becomes compressive as the IMC grows and then saturates. The saturation value does not depend primarily on the amount of IMC or its growth rate but rather on the relaxation processes in the Sn layer. Based on our stress measurements in Sn-based layers on Cu, relaxation is enhanced for layers with greater thickness, larger grain size and the addition of Pb. This was confirmed by directly measuring the relaxation of thermal stresses in similar layers of Sn on Si without the presence of Cu. The enhanced relaxation in layers with larger grain size and thickness is consistent with many other measurements on thin films that show greater relaxation for larger grained material. Pb in the alloy layers enhances relaxation by changing the microstructure from columnar to equi-axed so that there are horizontal grain boundaries that can act as sinks for diffusing atoms without inducing stress in the layer. For thin layers of Pb-Sn on Si that had a columnar microstructure, the relaxation of thermally induced stress was the same as for pure Sn layers.⁹

In samples that were annealed and/or reflowed, the thermal treatments

lead to a much thicker layer of IMC than for the untreated samples. However, the thicker IMC did not induce compressive stress because the sample became tensile as it was cooled due to the thermal-expansion mismatch with the substrate.

The major determinant of whisker formation was the amount of compressive stress in the film. This was true independently of the amount of IMC that formed, i.e., the stress could be less compressive if there was more relaxation (such as for larger grain size) or for the samples that were cooled after heat treatment. This was true for all the cases studied in this work: if the sample had more compressive stress, than the whisker density was higher.

These measurements provide some insight into the effectiveness of potential strategies to mitigate whisker formation. One method is to prevent the growth of IMC to prevent the generation of stress, for instance by the use of diffusion barriers such as Ni.²³ However, this is only a kinetic barrier and does not remove the driving force for IMC formation, so if the barrier is disrupted (e.g. by mechanical deformation or thermal cycling) then whisker formation can occur again. Another way to reduce whiskering is to lower the steady-state compressive stress

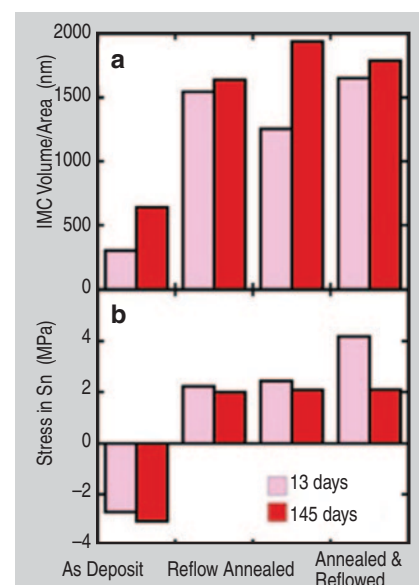


Figure 10. Measurements of (a) IMC volume, (b) Sn stress after 13 and 145 days on as deposited, reflowed, annealed, and annealed followed by reflowed samples with Sn thickness of 10 μm electroplated on top of 1 μm of copper layer.

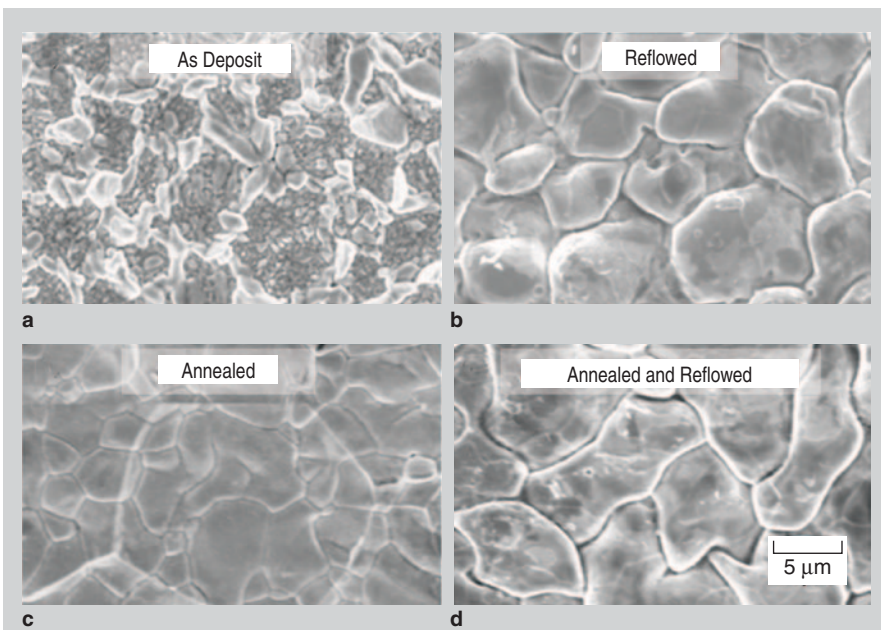


Figure 11. SEM images of Sn/Cu samples (Sn thickness of 10 μm electroplated on top of 1 μm of copper layer) after the Sn layer has been removed after 13 days from (a) as-deposited, (b) reflowed, (c) annealed, and (d) annealed followed by reflowed samples by etching. The bright spots in as-deposited sample correspond to particles of IMC, whereas a continuous film of IMC was formed on other samples.

level, thus reducing the driving force for whisker formation. This is consistent with the suppression of whiskering in Pb-Sn layers, where the presence of a more equiaxed microstructure with abundant oblique grain boundaries enhances the rate of stress relaxation via Coble creep.^{16,21} Sn-Bi²⁴ and other alloy additions²⁵ have also been investigated as a means to modify the microstructure and enhance stress relaxation in the Sn layer. An alternative method for enhancing stress relaxation may be weakening of the surface oxide and enabling the stress to relax by diffusion of atoms to the surface. Processes such as reflow and annealing suppress whiskering in two ways: the thermal expansion mismatch induces tensile stress in the layer when it is cooled after the thermal treatment. In addition, the heat treatment creates a thicker, more uniform IMC layer that reduces the rate of subsequent IMC growth after the initial processing. However, ultimately it does not remove the driving force for IMC formation and may only slow

down the formation of whiskers, not prevent them. Finding a material to replace Pb is difficult because many suggested methods (such as modifying the microstructure of the Sn) are not robust and will not persist after the material is heated to make a solder joint.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the support of the NSF-supported Brown MRSEC (DMR0079964), NSF (DMR0856229) and help from J. Wasserman, E. Buchovecky, A. Bower, L.B. Freund, S. Kumar, and G. Barr.

References

1. J.A. Brusse et al., in *Proc. 22nd Capacitor and Resistor Technology Symposium* (2002), pp. 67–80.
2. G.T. Galyon, *IEEE Trans. Electron. Pkg. Manu.*, 28 (2005), pp. 94–122.
3. NASA, Multiple Examples of Whisker-induced Failures are Documented on the NASA Website, nasa.gov/whisker/.
4. S.M. Arnold, *IEEE Electron. Comp. Technol. Conf.* (1959), pp. 75–82.
5. K.N. Tu and R.D. Thompson, *Acta Metall.*, 30 (1982), pp. 947–952.
6. J. Smetana, *IEEE Trans. Electron. Pkg. Manu.*, 30 (2007), pp. 11–22.

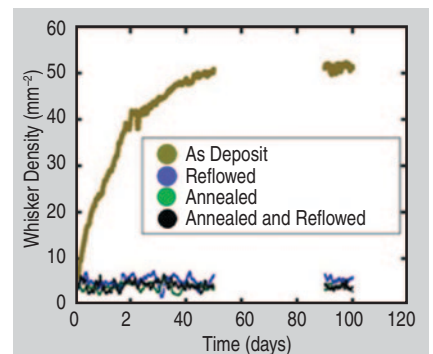


Figure 12. Measurements of whisker density on as-deposit, reflowed, annealed, and annealed followed by reflowed samples with a Sn thickness of 10 μm electroplated on top of 1 μm of copper layer.

7. B.Z. Lee and D.N. Lee, *Acta Mater.*, 46 (1998), pp. 3701–3714.
8. N. Jadhav et al., *IEEE Trans. Electron. Pkg. Manu.*, 33 (2010), pp. 183–192.
9. N. Jadhav et al., *J. Electron. Mater.* (accepted 2011).
10. N. Jadhav et al., *JOM*, 62 (7) (2010), pp. 30–37.
11. P. Oberndorff et al., “Intermetallic Formation in Relation to Tin Whiskers” (Paper presented at the IPC/Soldertec International Conference on Lead-Free Electronics, Brussels, 2003).
12. W. Zhang et al., *IEEE Trans. Electron. Pkg. Manu.*, 28 (2005), pp. 85–93.
13. E. Chason and J.A. Floro, *MRS Symposium Proceedings VI* (Pittsburgh, PA: MRS, 1997), pp. 417–422.
14. L.B. Freund and S. Suresh, *Thin Film Materials: Stress, Defect Formation and Surface Evolution*, 1st ed. (Cambridge, U.K.: Cambridge University Press, 2009), pp. 86–93.
15. E. Chason et al., *Appl. Phys. Lett.*, 92 (2008), p. 171901.
16. J.W. Shin and E. Chason, *J. Mater. Res.*, 24 (2009), pp. 1522–1528.
17. M. Onishi and H. Fujibuchi, *Trans. Jpn. Inst. Metals*, 16 (1975), pp. 539–547.
18. E. Buchovecky et al., *J. Electron. Mater.*, 38 (2009), pp. 2676–2684.
19. Y. Choi and S. Suresh, *Acta Mater.*, 50 (2002), pp. 1881–1893.
20. R.-M. Kelle et al., *J. Mater. Res.*, 13 (1998), pp. 1307–1317.
21. W.J. Boettinger et al., *Acta Mater.*, 53 (2005), pp. 5033–5050.
22. C.-F. Yu et al., *Microelectronics Reliability*, 50 (2010), pp. 1146–1151.
23. Y. Zhang et al., *Proc. IPC SMTA Council Apex* (Blackburn, IL: IPC—Association Connecting Electronics Industries, 2002), pp. S06-1–8.
24. E. Sandnes et al., *J. Electron. Mater.*, 37 (2008), pp. 490–497.
25. A. Rae and C.A. Handwerker, *Circuits Assembly*, 15 (2004), pp. 20–25.

Eric Chason, professor, Nitin Jadhav, post-doc, and Fei Pei, graduate student, are with the School of Engineering, Brown University, Providence, RI 02912, USA. Prof. Chason can be reached at eric_chason_phd@brown.edu.

Eric Chason and Nitin Jadhav are TMS Members!

To read more about them, turn to page 9. To join TMS, visit www.tms.org/Society/Membership.aspx.

TMS