Understanding Whisker Phenomenon - Driving Force For The Whisker Formation

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Abstract
The physical, chemical and structural properties of electroplated Sn and whiskers are studied using various techniques including X-Ray diffraction (XRD), Focussed Ion Beam (FIB), scanning Auger microscopy (SAM) and SEM/EDS. From the results of these studies we conclude that the driving force for the whisker formation is the compressive stress in the Sn coating. The tensile stress in the Sn coating, on the other hand, will hinder the whisker formation. This understanding provides the foundation for the whisker prevention remedies, which we offer to the electronic industry.

Introduction
Under environmental and competitive/marketing pressure, the electronics industry is seeking lead-free solders as replacement for tin/lead solders used in electronic manufacturing. Among several alternatives for surface finishes, electroplated pure tin may be the simplest process as a “drop-in” replacement for tin-lead as component finishes. However, fear of “whiskers” has been a major concern inhibiting its implementation. This is because tin whiskers, with a length from a few micrometers to several millimeters, may grow from electroplated Sn and cause electric shorts in electronic devices, particularly, in fine-pitch high I/O (input/output) components. For Sn to become a viable alternative, the whisker phenomena has to be understood and remedies for preventing whisker growth or reducing the growth rate to an acceptable level have to be established.

In our previous work,19-20 we introduced the concept of Whisker Index for quantifying the rate of whisker growth. Whisker Index (WI), defined as a function of number (n), length (L), and diameter (d) of the whiskers, is used to characterize the propensity of whisker growth for various Sn films. In this paper, we report our works in the understanding of the mechanisms of whisker growth, which are studied using various techniques including X-Ray diffraction (XRD), Focussed Ion Beam (FIB), scanning Auger microscopy (SAM) and SEM/EDS.

Experimental
Three pure tin finishes are used in this study: bright, matte and satin bright tin. The plated samples were subdivided into two groups:

Group 1: as-plated samples were aged at 25°C or 50°C.
Group 2: compressive or tensile-bent samples were aged at 25°C or 50°C.

All samples were examined via SEM at various magnifications and periodic intervals of time. To ensure statistical significance, an area of 0.5 mm x 27 mm was scanned for large whisker (length > 10 μm). For small whisker (length < 10 μm), 5 observation areas (0.18 mm x 0.24 mm/each) were used. Identical whisker counting procedures were used for all samples in these experiments. In the quantitative analysis, the number of whiskers was “manually” counted, and length and diameter were obtained from SEM photos.

To reveal the local structure of whiskers, cross sections along the root of the whisker are performed using focused ion beam (FIB). In a FIB experiment, an extremely small diameter beam of gallium ions is used to image the surface and locate the whisker. The same focused ion beam is then used to remove materials from the surface at high lateral resolution.
and cut through the whisker with accuracy better than 10 nm.

Internal stress in the Sn coating was measured using x-ray diffraction (XRD) and bent strip techniques. In a XRD experiment, the change of the lattice constant (strain) due to the stress is measured. The macro-stress can than be calculated from the measured strain. XRD provides means for non-destructive and local stress measurement. The real-time analysis of stress evaluation during the aging can also be performed. In the bent strip stress testing method, a thin metal strip is plated on one side of the strip. Depending on the type of stress (compressive or tensile), the strip will bend either in- or out-ward. The degree of bending correlates with the level of the stress in the coating. The biggest advantage of this method is that it can be used to measure the stress during the electroplating. However, the bent strip method measures an average stress over the entire strip and can not be easily used to monitor the stress evolution with the time during the sample aging.

Results
In Table 1, the whisker indexes for selected samples aged at 50°C up to ten months are summarized. The details of these results can be found in the previous papers.¹⁹-²⁰

<table>
<thead>
<tr>
<th>Table 1 - Whisker Index Calculations</th>
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<tr>
<td>4 Months</td>
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<tr>
<td>Bright</td>
</tr>
<tr>
<td>Bright Compressive</td>
</tr>
<tr>
<td>Bright Tensile</td>
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<tr>
<td>SB Sn</td>
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<td>SB Sn/Ni</td>
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</table>

Bright vs. Satin Bright
The whisker index data shown in Table 1 clearly demonstrate that the bright finish is much more prone to whisker formation than the satin bright finish. For instance, after 10 months aging at 50°C, the whisker index for the bright finish is about 6,300 times higher than that for the satin bright finish.

Effect of the Stress: Stress Generated During Plating vs. Stress Generated During Storage
It has been widely documented and agreed that the compressive stress is the driving force for the whisker growth.¹²-²⁵ The internal stress can either be introduced during the plating of the Sn film or generated during the sample aging. To determine the relative importance of the stress generated from these two different sources, the internal stress is measured using XRD immediately after plating as well as after 4 months aging at room temperature for a bright Sn and a satin bright Sn. This result is summarized in Table 2.

<table>
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<th>Table 2 - Internal stress (MPa) measured using XRD</th>
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<tr>
<td>As Plated</td>
</tr>
<tr>
<td>Bright</td>
</tr>
<tr>
<td>S B Sn</td>
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The as-plated samples have very low stress, with the satin bright Sn virtually stress free and the bright Sn being slightly compressive stressed. Similar results have been also obtained with the bent strip method, which shows a zero stress for a satin bright Sn and -4 MPa for a 3 μm thick bright Sn.

After aging the sample at room temperature for 4 months, there is a dramatic increase of the stress in both Sn coatings. The bright Sn shows a compressive stress of 10 MPa, while the SB Sn has a compressive stress of 7 MPa. The build-up of the compressive stress in the Sn coating is most likely related to the Sn-Cu interdiffusion at the interface (see FIB result in the next paragraph), which eventually leads to the whisker formation. Clearly, for bright and satin bright Sn plated under the condition used in our experiments, the stress generated during the storage (sample aging) plays the dominating role in determining the whisker growth.

Type of Stress: Compressive vs. Tensile
There is a general agreement on the role of the compressive stress with respect to the whisker growth.¹²-²⁵ On the other hand, very little is known about the role of the tensile stress. It has been generally assumed that the tensile stress also promotes the whisker growth but not as severe as the compressive stress. Due to the lack of systematic and quantitative studies of the whisker growth kinetics, there is no direct experimental support for this assumption. To study the effect of different types of stress on the whisker growth kinetic, we have applied compressive and tensile stress externally on the sample by bending the sample as shown in Figure 1.
whisker growth rate. On the other hand, the externally applied tensile stress reduces the rate of the whisker growth on a bright Sn coating.

To further understand why the tensile stress reduces the whisker growth, we have studied the local structure of the whisker using FIB. Figure 2 shows FIB images of a whisker found on a matte Sn, which was plated directly on a Cu substrate.

The sample was aged at room temperature for 13 months. The pictures in Figure 2 represent various stages of cutting through the whisker. Figure 2a is the FIB image of the surface taken after a trench is cut into the coating next to the whisker. FIB is then used to gradually cut through the whisker and FIB images were taken at various stages of cutting. These results are shown in Figures 2b and 2c. The grain structure around the whisker is nicely revealed in these images.

Three different layers can be identified in these images: Cu substrate, Sn-Cu intermetallic layer and Sn layer. The intermetallic growth at the Sn and Cu interface shows strong anisotropy, with some areas growing much faster than others. There are also a very clear grain boundary between the whisker and adjacent grains. The whiskers seem to originate from the middle of the Sn coating, rather than from the Sn-Cu interface or the Sn surface. Apparently, a whisker nucleates is formed within the Sn coating and then grows out of the Sn coating. There is no lateral growth of the whisker within the coating.

Very similar results have been also obtained for satin bright Sn plated on Cu substrate. Figure 3 shows a FIB image for a whisker found on the satin bright Sn, which was aged at room temperature for 18 months.

Here again, intermetallic compound formation is observed at Sn and Cu interface. Similar to the matte Sn, very clear grain boundary is observed between the whisker and adjacent grains and the whisker is originated within Sn film and grows out of the coating. No lateral growth within the coating is seen.
FIB experiments were also performed on bright Sn, which was plated over the Cu substrate. The sample was aged at room temperature for 18 months. Figure shows FIB images with increasing magnification from a to c. The length of this particular whisker is about 250 μm (Figure 4a). As Figure 4b and 4c show, the long filament-type whisker originates from the nodule on the surface. There is again a very clear grain boundary between the filament whisker and nodule whisker. The filament is not in direct contact with the original Sn coating but through the nodule. The mass transport from Sn film to the filament whisker, necessary for the formation of this very long whisker, occurs through the nodule whisker. The nodule whisker apparently acts as a precursor state for the formation of the filament whisker. This is consistent with the observation that the nodule whisker is seen before the filament whisker during the aging at room temperature as well as 50°C.

The most significant and common result in the FIB experiments for the three finishes is that the whisker only grows externally and there is no visible growth within the coating. This result is consistent with the conclusion drawn from kinetic study that the compressive stress promotes the whisker growth and tensile stress reduces the whisker growth.

**Effect of Ni Underlayer**

As discussed above, a compressive stress develops within the Sn coating with the time during the sample aging. The build-up of the compressive stress in the Sn coating is correlated to the preferential Cu diffusion into Sn at the Sn-Cu interface and is the driving force for the whisker formation from the pure Sn. To prevent the whisker formation, one has to stop Cu diffusion into Sn. One possibility is using a Ni-underlayer between the Cu-substrate and Sn-film. To assess the effectiveness of the Ni-underlayer in preventing the compressive stress building up in the Sn coating, we have measured the stress evolution of bright and satin bright Sn plated over a Ni-underlayer. Table 3 summarizes the stress results for the two finishes plated over Cu with and without Ni underlayer.

<table>
<thead>
<tr>
<th>Stress (Mpa)</th>
<th>Sn/Cu</th>
<th>Sn/Ni/Cu</th>
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<tbody>
<tr>
<td>Bright Sn</td>
<td>-10±1</td>
<td>9±1</td>
</tr>
<tr>
<td>SB Sn</td>
<td>-7±1</td>
<td>7±0</td>
</tr>
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</table>

The samples were aged at room temperature for 4 months. As discussed above, a compressive stress is seen for Sn plated directly over Cu. However, if a Ni-underlayer is used between Sn and Cu, a tensile stress is seen for both bright and SB Sn after 4 months aging. Consequently, we did not see any whisker growth from these coatings as illustrated in Figure 5, which compares whisker index for these finishes. It is evident from Figure 5 that the use of a Nickel underlayer effectively eliminates whisker formation.
from both bright and satin bright Sn finishes due to the tensile stress building up in the Sn coating.

![Image: Figure 5 - Effect of Ni-Underlayer on the Whisker Index for Bright and Satin Bright Sn](image)

**Discussions**

The mechanism of the whisker growth from electroplated Sn has been widely studied\(^{12-25}\). When Sn is plated directly over a Cu substrate, there will be intermetallic formation at the Cu-Sn interface with the time. It has been found that the intermetallic formation occurs by Cu diffusion into Sn. There is very little Sn diffusion into Cu. Furthermore, the diffusion front is not evenly distributed throughout the coating and dominated by the grain boundary diffusion\(^{25}\). There are areas where the intermetallic formation is fast and areas where it is slow. Since more matter is put into a fixed volume, a compressive stress is generated in the Sn film. The presence of Sn oxide prevents the stress from being released. With the time, this compressive stress keeps building up. Since the Sn oxide layer is not perfect, there is always some defect in the Sn oxide layer. When the compressive stress becomes high enough, it will break through the defect in the oxide layer and the whisker will form to release the compressive stress. Within the frame of this mechanism, the driving force is to remove the excessive materials (compressive stress) from the coating by growing the whisker. For a coating with the tensile stress (meaning that there is a deficiency of materials in the coating), the whisker growth (removing materials from coating) will further increase the tensile stress and therefore is thermodynamically unfavorable. On the other hand, the grain growth within the coating, which rearranges atoms within the coating, could reduces the tensile stress. Since only external whisker growth and no internal growth within the coating as illustrated by the FIB results, it is to conclude that the tensile stress reduces the propensity of the whisker growth.

This result is also confirmed by the kinetic study, where a tensile stress is imposed on the coating by mechanical bending. While the compressive-bent sample showed an increased whisker growth propensity compared to the non-bent sample, the tensile-bent sample showed a lower whisker index compared to the non-bent sample. The initial imposed tensile stress on the sample seems to slow down the build-up of the compressive stress in the coating but apparent did not completely stop it. The Cu diffusion into Sn eventually converts the initially tensile-stressed sample to a compressive-stressed sample, which leads to the whisker formation. The other possible explanation is that the externally applied tensile stress is not evenly distributed over the sample. Areas with low or no tensile stresses are subjected to quick compressive stress building up due to the Cu diffusion. It would be interesting to measure the stress evolution on the tensile-bent sample. Since the stress measurement using XRD requires a flat sample, it can not be used to measure the stress on the bent sample.

One of the most interesting findings in this work is the ability of a Ni-underlayer to impose a tensile stress on a Sn coating and therefore stop the whisker growth. As discussed above, a compressive stress will develop with the time in the Sn coating when plated over Cu and a tensile stress will build up in the Sn film when plated over Ni. This difference is ultimately responsible for the spontaneous whisker growth from Sn plated over Cu and no whisker growth for Sn plated over Ni. The formation of the compressive stress can be explained by the much faster diffusion rate of Cu into Sn compared to the diffusion rate of Sn into Cu. As a result, there is an excessive material in the Sn film and the build-up of the compressive stress. At room temperature, the solubility of Ni in Sn is less than 0.005% Ni (atomic). On the other hand, the solubility limit of Sn in Ni determined from the Curie points is 9.7% Sn (atomic)\(^{26}\). These large difference in the solubility would suggest that there will be more Sn diffusion into Ni than Ni diffusion into Sn. Consequently, with the time there will be a deficiency of material in the Sn coating and the tensile stress will form in the Sn film. Experiments are under way in our lab to directly measure the relative diffusion rate of Ni versus Sn at the Sn-Cu interface.

**Recommendations**

In summary, our observations indicate that internal stress is the key factor in determining the whisker growth: the compressive stress drives the whisker growth and tensile stress reduces the propensity of the whisker growth. The interfacial diffusion between Sn and the substrate/underlayer determines the type of the stress generated in the coating with the time and controls the whisker growth propensity. Based on this understanding, we offer following recommendations to the electronics industries:
• a) To archive maximal whisker protection, large grain Sn with no compressive stress should be used. If the substrate contains Cu, a Ni-underlayer should be used.

• b) If the use of a Ni-underlayer is prohibited in an application, reflow may be used. Reflow reduces or delays the whisker growth by releasing the stress in the coating as well as forming a Sn-Cu intermetallic layer between Cu and Sn. This intermetallic layer acts as a barrier to slow down the further diffusion of Cu into Sn.

• c) A thick Sn coating can also be used to reduce the whisker growth propensity, since it will take longer time for Cu to diffuse to near-surface area generating compressive stress.

• d) Last but not least, the stress evolution with the time should be monitored if a new process is installed. If the compressive stress is building up in the Sn layer with the time, it is very likely that whisker will eventually form on the surface. On the other hand, if there is a tensile stress building up or no stress building up with the time, no whisker will form on the surface.

References