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OVERVIEW

Mechanism and Prevention of Spontaneous Tin Whisker Growth

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Spontaneous Sn whisker growth on Cu leadframe finished with Pb-free solder is a serious reliability problem in electrical and electronic devices. Recently, Fortune magazine had an article to describe the urgency of the problem. The spontaneous growth is an irreversible process, in which there are two atomic fluxes driven by two kinds of driving force. There are a flux of Cu atoms and a flux of Sn atoms. The Cu atoms diffuse from the leadframe into the solder finish driven by chemical potential gradient to form intermetallic compound of Cu_6Sn_5 in the grain boundaries of the solder, and the growth of the compound at room temperature generates a compressive stress in the solder. To relieve the stress, a flux of Sn atoms driven by the stress gradient diffuses away to grow a spontaneous Sn whisker which is stress-free. The typical industry solution is to insert a diffusion barrier of Ni between the Cu and solder to prevent the diffusion of Cu into the solder. It is insufficient, because we have to uncouple the irreversible processes and stop both the fluxes of Cu and Sn. A solution is presented here.

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1. Introduction

Spontaneous beta-tin (Sn) whisker growth is known to occur readily on matte Sn finishes on Cu electrodes. Today, because of the wide-spread applications of Pb-free solders on Cu conductors in electronic packaging of consumer electronic products, Sn whisker growth has become a serious reliability issue because Pb-free solders are Sn-based.[1–3] Reference 1) is an article in Fortune magazine which has described the problem very well. In fact, a Sn whisker has killed a Galaxy 4 communications satellite. The issue of whisker growth concerns mainly the Cu leadframes used on surface mount technology of electronic packaging. The leadframes are finished with a layer of eutectic SnCu or pure Sn solder for surface passivation and for enhancing wetting reaction when the leadframe is joined to a printed circuit board, yet whiskers of Sn are frequently observed on the finishes. Some whiskers can grow to several hundred microns in length, which are long enough to become electrical shorts between neighboring legs of a leadframe.

Figure 1 is an SEM image of Sn whiskers grown on a eutectic SnCu finished Cu leadframe. Many long Sn whiskers have been found and one of them as shown in the figure is long enough to short two neighboring legs of the leadframe. When there is a high electrical field across the narrow gap between the tip of a whisker and the point of contact on the other leg, a spark may occur and can ignite fire just before the tip of the whisker touching the other leg. The fire may result in failure of a device or a satellite.[1–3] Another mode of failure is a broken whisker falling and bridging the gap between two electric contacts.

Whisker growth is a surface relief phenomenon. Tin whisker is one of the most well known cases.[4–21] While it is a very old subject, there is currently a renewed interest in the mechanism and prevention of Sn whisker growth owing to the application of Pb-free solders in electronic manufacturing. To understand the mechanism of whisker growth, we note that spontaneous whisker growth can be regarded as a creep process in which both stress generation and stress relaxation occur simultaneously at room temperature. Because there are two kinetic processes, we can also regard it as an irreversible process. We find that (1) The room temperature self grain boundary diffusion of Sn in Sn, (2) The room temperature diffusion of Cu into Sn and the reaction between the Cu and Sn to form Cu_6Sn_5, which caused the compressive stress in the Sn, and (3) The stable and protective surface Sn oxide are the three necessary and sufficient conditions for whisker growth.[22] We have used cross-sectional scanning and transmission electron microscopy to examine Sn whiskers, with samples prepared by focused ion beam thinning.[23] Also we have used X-ray micro-diffraction in synchrotron radiation to study the structure and stress distribution around the root of a whisker grown on eutectic SnCu.[24]

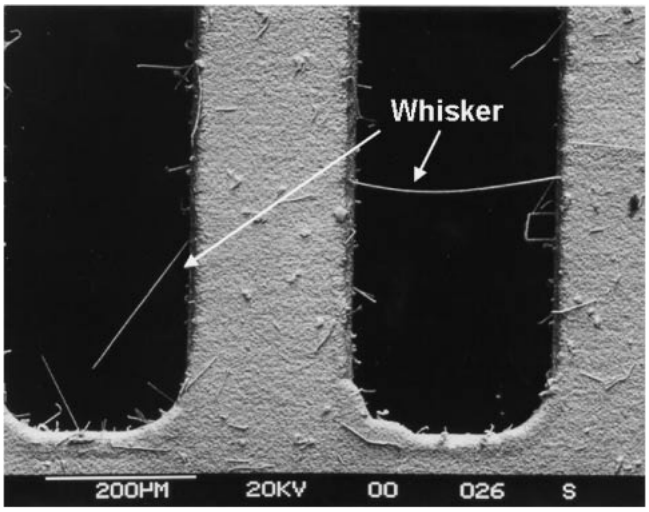

Fig. 1 An SEM image of Sn whiskers grown on a eutectic SnCu finished Cu leadframe.

In Fig. 2(a), an enlarged SEM image of a long whisker on the eutectic SnCu finish is shown. The whisker in Fig. 2(a) is straight and its surface is fluted. The crystal structure of Sn is

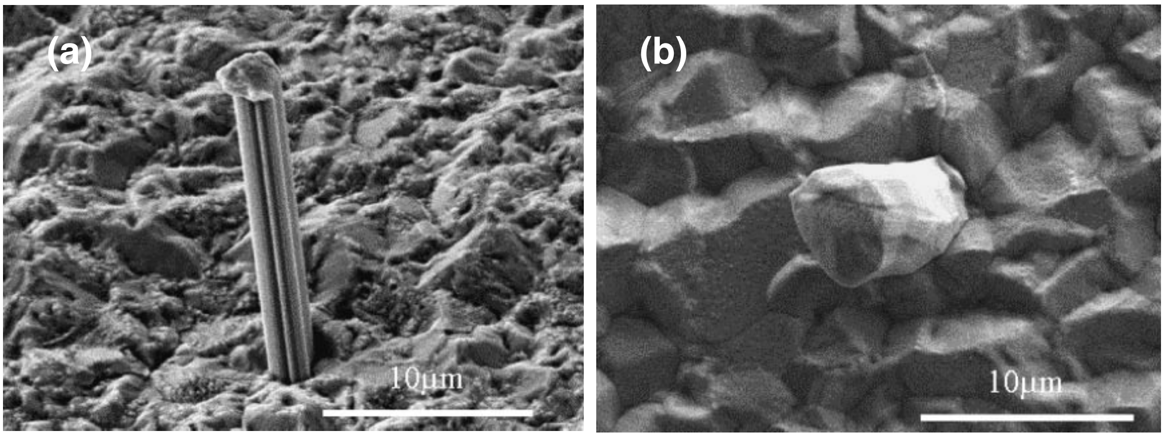

Fig. 2 (a) An enlarged SEM image of a long whisker on the eutectic SnCu finish is shown. (b) On the pure or matte Sn finish surface, short whiskers were observed as shown.

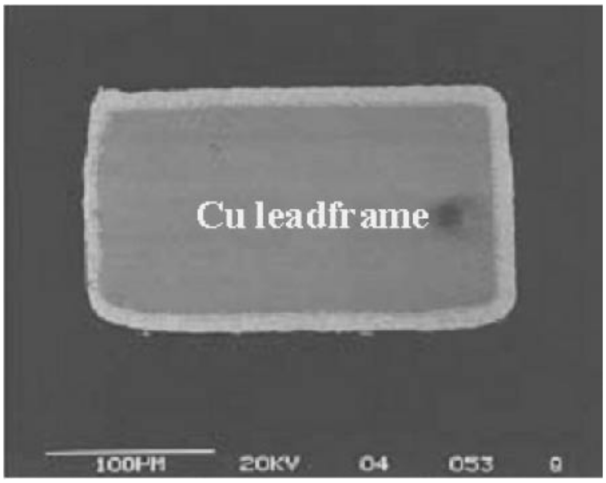

Fig. 3 Cross-sectional SEM image of a leadframe leg with SnCu finish is shown.

body-centered tetragonal with the lattice constant "a" = 0.58311 nm and "c" = 0.31817 nm. The whisker growth direction, or the axis along the length of the whisker, has been found mostly to be the "c" axis.

On the pure or matte Sn finish surface, short whiskers were observed as shown in Fig. 2(b). The surface of the whisker in Fig. 2(b) is faceted. Besides the difference in morphology, the rate of whisker growth on the pure Sn finish is much slower than that on the SnCu finish. The direction of whisker growth on the matte Sn is more random too.

Comparing the whiskers formed on SnCu and pure Sn, as shown in Figs. 2(a) and (b), it seems that the Cu in eutectic SnCu has enhanced Sn whisker growth. Although the composition of eutectic SnCu consists of 98.7 at% of Sn and 1.3 at% of Cu, the small amount of Cu seems to have caused a very large effect on whisker growth on the eutectic SnCu finish.

In Fig. 3, a cross-sectional SEM image of a leadframe leg with SnCu finish is shown. The rectangular core of Cu is surrounded by an approximate 15 μm thick of SnCu finish. A higher magnification image of the interface between the SnCu and the Cu, prepared by focused ion beam polishing, is shown in Fig. 4(a). An irregular layer of Cu_6Sn_5 compound can be seen between the Cu and SnCu. The grain size in the SnCu finish is about several microns. More importantly, there are Cu_6Sn_5 precipitates in the grain boundaries of SnCu. The grain boundary precipitation of Cu_6Sn_5 is the source of stress generation in the SnCu finish. It provides the driving force of spontaneous Sn whisker growth. We shall address this critical stress issue later. In Fig. 4(b) a similar image of the interface between matte Sn and Cu is shown. A much less amount of grain boundary precipitation of Cu_6Sn_5 is found. This is the major microstructure difference between the eutectic SnCu and the matte Sn finishes. The microstructure difference as shown in Figs. 4(a) and (b) is strongly correlated to the size difference of Sn whiskers grown on the finish surfaces as shown in Figs. 2(a) and (b).

In this paper, we shall first review the irreversible processes of stress generation and stress relaxation and their combination that leads to the growth of Sn whiskers. Then we shall review briefly the measurement of stress gradient in the Sn grains surrounding the root of a Sn whisker and a simple kinetic model of the growth of a Sn whisker. Finally, a solution for the prevention of Sn whisker growth will be presented.

2. Irreversible Process in Spontaneous Sn Whisker Growth

2.1 The stress generation (driving force) in Sn whisker growth

The whisker of Sn is known to grow from the bottom, not from the top. This is deduced from the fact that the morphology of the tip does not change during the growth.[8] Also for a bent whisker, the part of the whisker below the bent grows longer, not the part above the bent. So a whisker is being pushed out by compression, similar to making spaghetti. The origin of the compressive stress can be mechanical, thermal, and chemical. But the mechanical and thermal stresses tend to be finite in magnitude, so they cannot sustain a spontaneous or continuous growth of whiskers for a long time. The chemical force is essential. The origin of the chemical force is due to the room temperature reaction between Sn and Cu to form the intermetallic compound (IMC) of Cu_6Sn_5.[17,25] The chemical reaction provides a

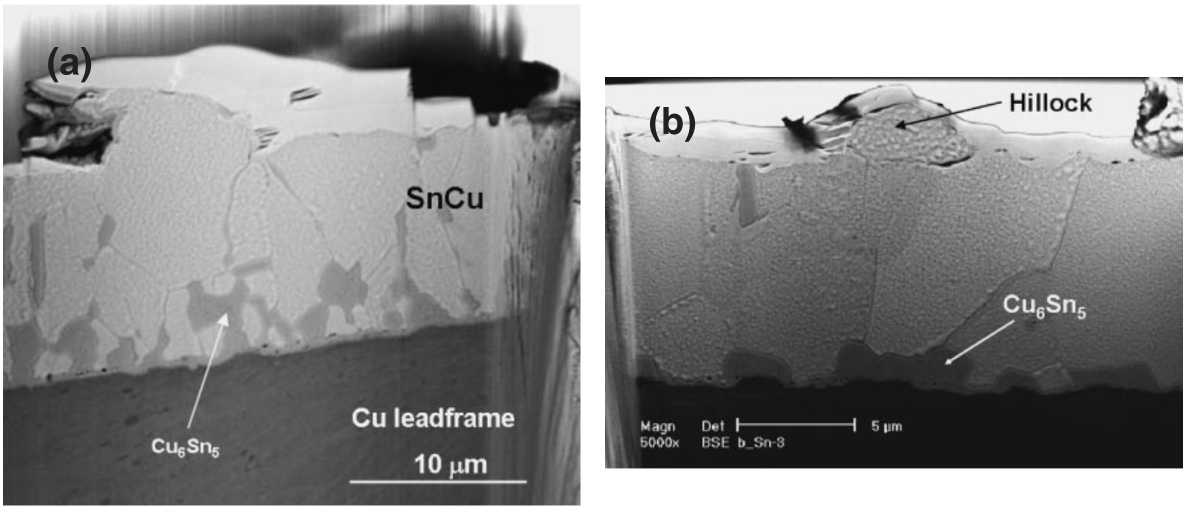

Fig. 4 (a) A higher magnification image of the interface between the SnCu and Cu layers, prepared by focused ion beam. Grain boundary precipitates of Cu_6Sn_5 are shown. (b) Same kind of image of he interface between matte Sn and Cu. A much less groan boundary precipitates is found.

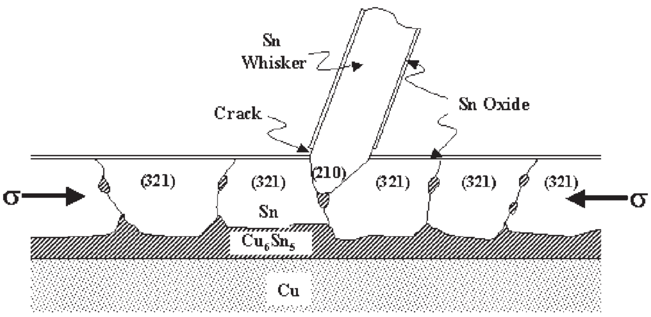

Fig. 5 We consider a fixed volume "V" in the Sn finish that contains a grain boundary precipitate of IMC and the stress induced due to the in-diffusion of a Cu atom.

sustained driving force for spontaneous growth of whiskers, as long as the reaction keeps going with unreacted Sn and Cu.

Stress is generated by interstitial diffusion of Cu into Sn and the formation of IMC in the grain boundary of Sn, as shown in Fig. 4(a). The volume increase due to the IMC growth will exert a compressive stress to the grains on both sides of the grain boundary. In Fig. 5, if we consider a fixed volume "V" in the Sn finish that contains a grain boundary precipitate of IMC, the growth of the IMC due to the diffusion of a Cu atom into this volume to react with Sn will produce a stress, $\sigma = -B(\Omega/V)$, where σ is the stress generated, B is bulk modulus, Ω is the partial molecular volume of a Cu atom in Cu_6Sn_5 (we ignore the molar volume change of Sn atoms in the reaction for simplicity). The negative sign indicates that the stress is compressive. In other words, we are adding an atomic volume into the fixed volume. When more and more Cu atoms, say "n" Cu atoms, diffuse into the volume, V, to form Cu_6Sn_5, the stress in the above equation of σ increases by changing Ω to $n\Omega$.

In the classic Kirkendall effect of interdiffusion in a bulk diffusion couple of A and B, the atomic flux of A is not equal to the opposite flux of B. If we assume that A diffuses into B faster than B diffuses into A, we might expect that there will be a compressive stress in B since there are more A atoms diffusing into it than B atoms diffusing out of it. However, in Darken's analysis of interdiffusion, there is no stress generated in either A or B. Why? But Darken has made a key assumption that vacancy concentration is in equilibrium everywhere in the sample.[26,27] To achieve vacancy equilibrium, we must assume that vacancies (or lattice sites) can be created and/or annihilated in both A and B as needed kinetically. Hence, provided that the lattice sites in B can be added to accommodate the incoming A atoms, there is no stress. The addition of a large number of lattice sites implies an increase in lattice planes if we assume that the mechanism of vacancy creation and/or annihilation is by dislocation climb mechanism. It further implies that lattice plane can migrate, which is the origin of marker motion if markers are embedded in the moving lattice planes in the sample. Hence, we have the marker motion equation in Darken's analysis. However, we must recall that in some cases of interdiffusion in bulk diffusion couples, vacancy may not be in equilibrium everywhere in the sample, so very often Kirkendall void formation has been found due to the existence of excess vacancies.[28]

For the fixed volume of V in the finish as considered in Fig. 5, to absorb the added atomic volume due to the in-diffusion of Cu, we must be able to add lattice sites in the fixed volume. Furthermore, we must allow the added lattice plane to migrate,[27] otherwise, compressive stress will be generated if the lattice planes cannot migrate. Since Sn has a native and protective oxide on the surface, the interface between the Sn and its oxide is a poor source and sink for vacancies and also the oxide ties down the lattice plane in Sn and prevent them from moving. This is the basic mechanism of stress generation in spontaneous Sn whisker growth. In this mechanism, we have ignored the diffusion of Sn into the Cu leadframes since Cu_6Sn_5 serves as the diffusion barrer of Sn. However, Cu_6Sn_5 is not a diffusion barrier to Cu.

Sometimes it is puzzling to find that Sn whiskers seem to grow on a tensile region of a Sn finish. For example, when a Cu leadframe surface was plated with eutectic SnCu, the initial stress state of the SnCu layer right after plating was tensile, yet whisker growth was observed. If we consider the cross-section of a Cu leadframe leg coated with a layer of Sn as shown in Fig. 3, the leadframe experienced a heat-treatment of reflow from room temperature to 250°C and back to room temperature. Since Sn has a higher thermal expansion coefficient than Cu, the Sn finish should be under tension at room temperature after the reflow cycle. Yet with time, Sn whisker grows, so it seems that Sn whisker grows under tension. Furthermore, if a leg is bent mechanically, one side of it will be in tension and the other side in compression. It is surprising to find that whiskers grow on both sides, whether the side is under compression or tension. These phenomena are hard to understand until we recognize that the thermal stress or the mechanical stress, whether it is tensile or compressive, is finite. It can be relaxed or overcome quickly by atomic diffusion at room temperature in the Sn. After that, the continuing chemical reaction will develop the compressive stress needed to grow whiskers. So the chemical force is essential and persistent. Room temperature reaction between Sn and Cu was studied by using thin film samples.[17,25]

2.2 The stress relaxation (kinetic process) in Sn whisker growth

Whisker growth is a unique creep phenomenon in which stress generation and stress relaxation occurs simultaneously. Therefore, we must consider two kinetic processes of stress generation and stress relaxation and their coupling by an irreversible process.[18] About the two kinetic processes, the first is the diffusion of Cu from the leadframe into the Sn finish to form grain boundary precipitates of Cu_6Sn_5, driven by a chemical potential gradient. The second is the diffusion of Sn from the stressed region to the root of a whisker to relieve the stress, driven by a compressive stress gradient. The distance of diffusion in the second process is much longer than the first and also the diffusivity in the second process is slower too, so the second process tends to control the rate in the spontaneous growth of whiskers.

Since the reaction of Sn and Cu occurs at room temperature, the spontaneous reaction continues as long as there are unreacted Sn and Cu. The stress in the Sn will increase with the growth of Cu_6Sn_5 in it. Yet the stress cannot build up forever; and it must be relaxed. Consequently, either the added lattice planes in the volume, V, in Fig. 5 must migrate out of the volume, or some Sn atoms will have to diffuse out of the volume to a stress-free region, *i.e.*, a whisker.

Since room temperature is a relatively high homologous temperature for Sn, which melts at 232°C, the self-diffusion of Sn along Sn grain boundaries is fast at room temperature. Therefore the compressive stress in the Sn induced by the chemical reaction at room temperature can also be relaxed at room temperature by atomic rearrangement via self grain boundary diffusion. The relaxation occurs by the removal of atomic layers of Sn normal to the stress, and these Sn atoms can diffuse along grain boundaries to the root of a stress-free whisker to feed its growth. We must ask why the process of stress relaxation occurs via whisker growth.

In an ultra-high vacuum, no surface hillocks of Al were found to grow on Al surfaces under compression.[29] Hillocks grow on Al surfaces only when the Al surface is oxidized, and the Al surface oxide is known to be protective. Without surface oxide, the free surface of Al is a good source and sink of vacancies, so a compressive stress can be relieved uniformly on the entire surface of the Al, based on Nabarro–Herring model of lattice creep or Coble model of grain boundary creep. In these models, as shown in Fig. 6, the relaxation can occur in each of the grains by atomic diffusion to the free surface of each grain. The free surfaces are effective source and sink of vacancies. Therefore, the relaxation is uniform over the entire Al film surface; all the grains just thicken slightly. Consequently, no localized growth of hillocks or whiskers will take place.

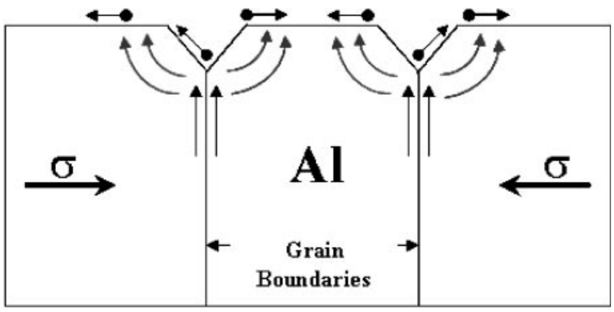

Fig. 6 A schematic diagram to show that when the surface has no oxide, the relaxation of stress can occur in each of the grains by atomic diffusion to the free surface of each grain.

We note that a whisker or hillock is a localized growth on an oxidized surface. Whiskers are local eruptions on the oxidized surface. To have a localized growth, the surface cannot be free of oxide, and the oxide must be a protective oxide so that it can effectively block all the vacancy sources and sinks on the surface. Furthermore, a protective oxide also means that it pins down the lattice planes in the matrix of Al (or Sn), so that no lattice plane migration can occur to relax the stress in the volume, V, considered in Fig. 5. Only those metals which grow protective oxides, such as Al and Sn, are known to have hillock or whisker growth. When they are in thin film or thin layer form, the surface oxide can pin down the lattice planes in the near-surface layer easily. On the other hand, if the surface oxide is very thick, it will physically block the growth of any hillock and whisker. No hillocks or whiskers can penetrate a very thick oxide. Thus, a necessary condition of whisker growth is that the protective surface oxide must not be too thick so that it can be broken at certain weak spots on the surface, and from these spots whiskers grow to relief the stress.

In Fig. 7(a), a focused ion beam image of a group of whiskers on the SnCu finish is shown. In Fig. 7(b), the oxide on a rectangular area of the surface of the finish was sputtered away by using a glancing incidence ion beam to expose the microstructure beneath the oxide. In Fig. 7(c), a higher magnification image of the sputtered area is shown, in which the microstructure of Sn grains and grain boundary precipitates of Cu_6Sn_5 are clear. Due to the ion channeling effect, some of the Sn grains appear darker than the others. The Cu_6Sn_5 particles distribute mainly along grain boundaries in the Sn matrix, and they are brighter than the Sn grains due to less ion channeling. The diameter of the whiskers is about a few microns. It is comparable to the grain size in the SnCu finish.

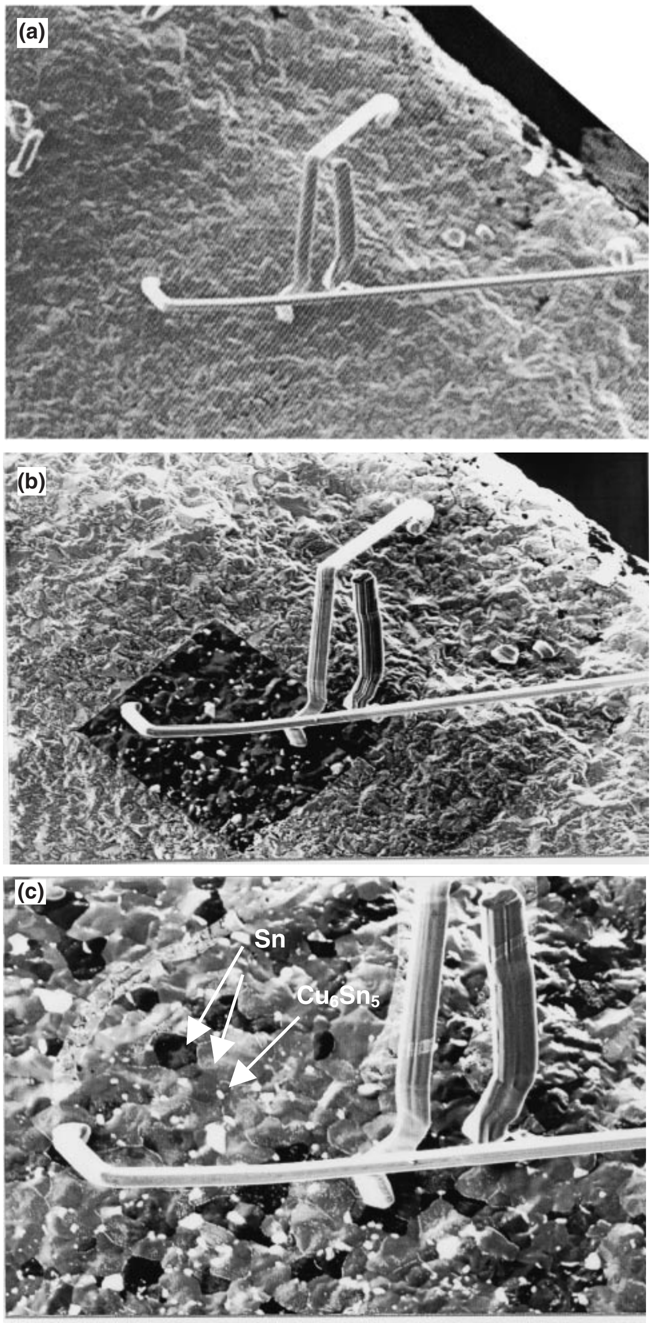

Fig. 7 (a) A focused ion beam image of a group of whiskers on the SnCu finish is shown. (b) The oxide on a rectangular area of the surface of the finish was sputtered away by using a glancing incidence ion beam to expose the microstructure beneath the oxide. (c) A higher magnification image of the sputtered area is shown, in which the microstructure of Sn grains and grain boundary precipitates of Cu_6Sn_5 are clear.

In ambient, we assume that the surface of the finish and every whisker is covered with oxide. The growth of a whisker has to break the oxide. The stress that is needed to break the oxide may be the minimum stress needed to grow whiskers. It seems that the easiest place to break the oxide is at the base of the whisker. Then to maintain the growth, the break must remain oxide-free so that it behaves like a free surface and vacancies can be supplied continuously and can diffuse into the Sn layer to sustain the long range diffusion of the Sn atoms needed to grow the whisker. In Fig. 5, we depict that the entire surface of the whisker is oxidized, except the base. The surface oxide of the whisker serves the very important purpose of confinement so that the whisker growth is essentially a one-dimensional growth.

The surface oxide of the whisker prevents it from growing in lateral direction, thus it grows with a constant cross-section and has the shape of a pencil. Also the oxidized surface may explain why the diameter of a Sn whisker is just a few microns. This is because the gain in strain energy reduction in whisker growth is balanced by the formation of surface of the whisker. By balancing the strain energy against the surface energy in a unit length of the whisker, $\pi R^2 \varepsilon = 2\pi R\gamma$, we find that $R = 2\gamma/\varepsilon$, where R is radius of the whisker, γ is surface energy per unit area, and ε is strain energy per unit volume. Since strain energy per atom is about four to five orders of magnitude smaller than the chemical bond energy or surface energy per atom of the oxide, the radius or diameter of a whisker is found to be several microns, which are about four orders of magnitude larger than the atomic diameter of Sn.

The growth of a whisker occurs at the root; it is being pushing out. We ask what is the growth mechanism? When Sn atoms diffuse to the root of a whisker, how can they be incorporated into the root of a whisker? The growth can be regarded as grain growth because the whisker is a single crystal and it grows longer with time. In the classical model of normal grain growth, the basic process is grain boundary migration against its curvature by atoms jumping from one grain across a grain boundary to the grain on the other side of the grain boundary.[30] Yet in whisker growth, it is unclear if there is grain boundary migration at the root. Using a serious of cross-sectional SEM images, the microstructure of the root of a whisker and its surrounding grains have been observed.[22] It suggests that most likely there is no migration of the grain boundaries between the whisker and the surrounding grains during the growth of the whisker. Whisker growth is a kind of grain growth with very little grain boundary migration. It seems that Sn atoms arriving in the root region along grain boundaries can be incorporated into the root of a whisker without jump across a grain boundary as in normal grain growth. This is because the Sn atoms are already diffusing in grain boundaries. Hence no grain boundary migration is needed. The atomistic model of incorporation of the atom into the whisker for its growth requires more study; it may take place at the kink sites on the bottom side of the whisker, similar to step-wise growth on a free crystal surface in epitaxial growth of thin films. We must mention that there are vacancies coming in from the surface crack at the root area to assist the growth.

To study the grain boundary structure around the root of a whisker, we have prepared cross-sectional TEM samples for direct observation of the root of a whisker. Figure 8 is an SEM image of the preparation of cross-sectional TEM samples by using focused ion beam etching. Focused ion beam was used to etch two rectangular holes into the finish separated by a thin wall as shown in Fig. 8. The location of the two holes was selected to have a whisker on top of the wall between them. After etching, the thickness of the wall is less than 100 nm so that it is transparent to 100 KeV electrons. The thin wall or foil contains a thin vertical section of the whisker, the root of the whisker, and a couple

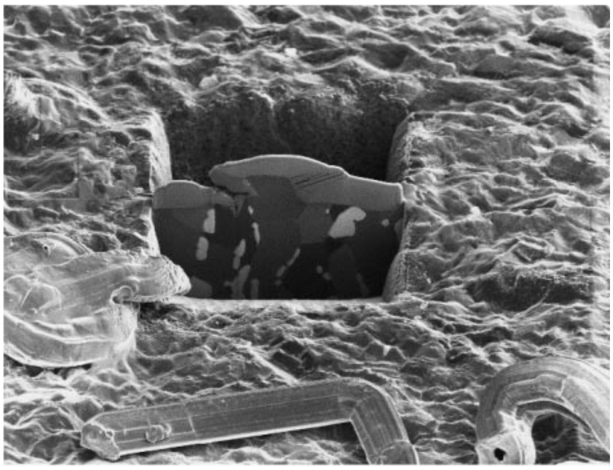

Fig. 8 A low magnification picture of an area of finish wherein a whisker is circled and scanned.

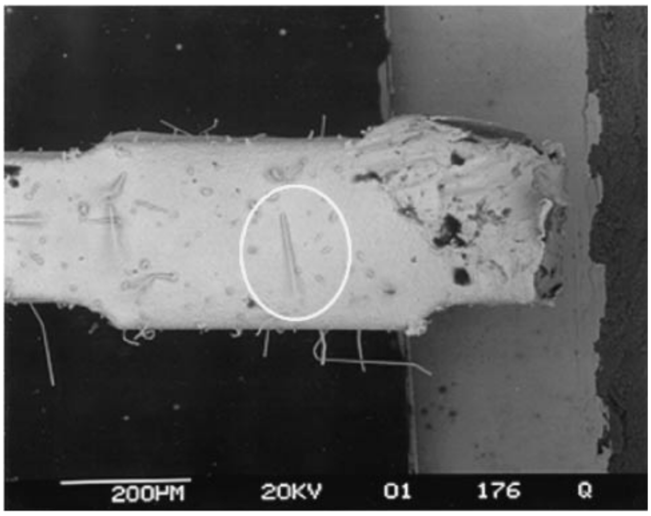

Fig. 10 Cross-sectional TEM image of the root of a Sn whisker.

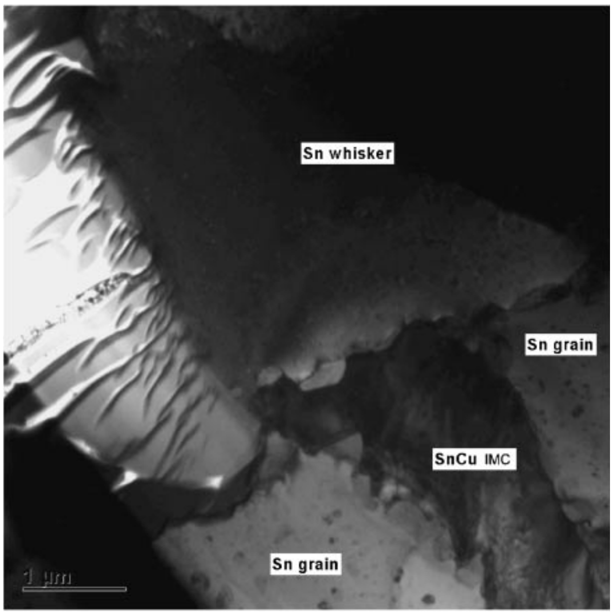

Fig. 9 Focused ion beam preparation of cross-section TEM samples.

grains surrounding the whisker. Figure 9 is a bright-field TEM image of a grain boundary between a whisker and a neighboring grain in the root region of the whisker.

Sometimes the surface of a whisker has the appearance of very fine saw-tooth steps. It indicates that the growth of the whisker may have the racked motion instead of a smooth motion. The racked motion may be due to a repetitive breaking of the oxide at the root of the whisker. The growth of the whisker has to break the oxide and exposes a free surface. Yet the free surface in ambient will form oxide right away, so the oxide has to be broken repetitively. No doubt, the atomistic mechanism of the growth of a whisker will require more experimental study and analysis.

3. Measurement of Stress by Synchrotron Radiation Micro-diffraction

The micro-diffraction apparatus in Advanced Light Source, at Lawrence Berkeley National Laboratory, was used to study Sn whiskers grown on SnCu finish on Cu leadframe at room temperature.[24)] The white radiation beam was 0.8 to 1 μm in diameter and the beam step-scanned over an area of 100 μm by 100 μm at steps of 1 μm. Several areas of the SnCu finish were scanned and those areas were chosen so that in each of them there was a whisker, especially the areas that contained the root of a whisker. During the scan, the whisker, and each grain in the scanned area, can be treated as a single crystal to the beam. This is because the grain size is larger than the beam diameter. At each step of the scan, a Laue pattern of a single crystal is obtained. The crystal orientation and the lattice parameters of the Sn whisker and the grains of SnCu matrix surrounding the root of the whisker were measured by the Laue patterns. The software in ALS is capable of determining the orientation of each of the grains, and displaying the distribution of the major axis of these grains. Using the lattice parameters of the whisker as stress-free internal reference, the strain or stress in the grains in the SnCu matrix can be determined and displayed. Figure 10 shows a low magnification picture of an area of finish wherein a whisker is circled and scanned.

The X-ray micro-diffraction study shows that at a local area of $100\,\mu m \times 100\,\mu m$, the stress is highly inhomogeneous with local variations from grain to grain. The finish is therefore under a biaxial stress only on the average. This is because each whisker has relaxed the stress in the region surrounding it. But, the stress gradient or stress distribution around the root of a whisker does not have a radial symmetry. The numerical value, and the distribution of stress, are shown in Table 1, where the root of the whisker is at the coordinates of "$x = -0.8415$" and "$y = -0.5475$". Overall, the compressive stress is quite low, of the order of several MPa; however, we can still see the slight stress gradient going from the whisker root area to the surroundings. It means that the stress level just below the whisker is slightly less compressive than the surrounding area. This is because the stress near the whisker has been relaxed by whisker growth. In Table 1, the long and dark-colored arrows indicate the directions of stress gradient. In the Table, some blocks or grids next to

Table 1 Stress distribution around the root of a whisker, which is at the coordinates of "$x = -0.8415$" and "$y = -0.5475$".

1.5 µm

(Unit : Mpa)

	-0.5400	-0.5415	-0.5430	-0.5445	-0.5460	-0.5475	-0.5490	-0.5505	-0.5520	-0.5535	-0.5550
-0.8340	-2.82	-3.21	-2.26	0.93	0.93	-0.23	-8.17	2.22	1.49	1.6	-0.03
-0.8355	-2.26	-2.64	-2.64	-1.04	1.37	1.37	-1.31	0.87	0.87	0.87	-0.7
-0.8370	-2.53	-3.21	-3.21	-2.64	-1.04	3.61	0.75	0.87	0.7	0.7	-0.19
-0.8385	-7.37	-9.62	-6.57	-2.64	3.61	4.52	3.61	0.29	-1.31	0	-4.79
-0.8400	-7.37	-8.22	-6.57	-1.18	0.75	4.23	0.75	-2.25	-2.27	-2.91	-6.91
-0.8415	-4.17	-4.8[illegible]	-4.17	-1.81	-0.67	0.00	-1.96	-1.96	-3.74	-5.08	-5.08
-0.8430	-4.17	-4.17	-3.63	-1.81	-1.81	-2.29	-2.29	-1.96	-1.96	-3.27	-3.27
-0.8445	-4.14	-4.17	-3.86	-3.63	-2.79	-4.64	-4.78	-0.84	-1.4	-1.49	-3.27
-0.8460	-3.14	-3.63	-3.86	-3.63	-3.13	-4.78	-4.78	0.04	0.04	-1.41	-2.33
-0.8475	-4.1[illegible]	-4.49	-4.49	-4.64	-3.86	-6.04	-1.72	3.55	3.55	-0.41	-2.33
-0.8490	-3.33	-5.67	-6.2[illegible]	-6.29	-2.66	-2.08	-1.72	-1.79	0	-1.79	-3.73

Whisker

each other show the similar stress level, which might mean that they belong to the same grain. No very long range stress gradient has been observed around the root of a whisker, indicating that the growth of a whisker has only relaxed most of the local compressive stress in the distance of several surrounding grains.

4. Kinetic Analysis of Sn Whisker Growth

To analyze the growth kinetics of a whisker, we assume a 2-dimensional model in cylindrical coordination. The whiskers are assumed to have a regular arrangement so that each occupies a diffusional field of diameter of 2b, as shown in Fig. 11. We further assume that the whisker has a constant diameter of 2a and a separation of 2b, and it has a steady-state growth in the diffusional field which can be described by a 2-dimensional continuity equation.[18] We recall that stress can be regarded as an energy density and a density function obeys the continuity equation.

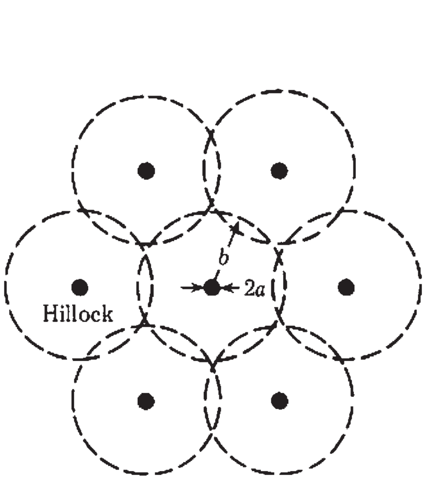

Fig. 11 Schematic diagram depicting a 2-dimensional distribution of Sn whiskers.

$$\nabla^2\sigma = \frac{\partial^2\sigma}{\partial r^2} + \frac{1}{r}\frac{\partial\sigma}{\partial r} = 0$$

The boundary conditions are

$$\sigma = \sigma_0 \text{ at } r = b, \quad \text{and} \quad \sigma = 0 \text{ at } r = a.$$

The solution is $\sigma = B\sigma_0 \ln(r/a)$, where $B = [\ln(b/a)]^{-1}$ and σ_0 is the average stress in the Sn film. Knowing the stress distribution, we can evaluate the driving force,

$$X_r = -\frac{\partial\sigma\Omega}{\partial r}$$

Then the flux to grow the whisker is calculated at $r = a$,

$$J = C\frac{D}{kT}X_r = \frac{B\sigma_0 D}{kTa}$$

We note that in a pure metal, $C = 1/\Omega$. The volume of materials transported to the root of the whisker is a period of dt is

$$JAdt\Omega = \pi a^2 dh$$

Where $A = 2\pi as$ is the peripheral area of the growth step at the root, s is the step height, and dh is the increment of height of the whisker in dt. Therefore, the growth rate of the whisker is

$$\frac{dh}{dt} = \frac{2}{\ln(b/a)}\frac{\sigma_0\Omega sD}{kTa^2}$$

To evaluate the whisker growth rate, we take $a = 3\,\mu\text{m}$, $b = 0.1\,\text{mm}$, $\sigma_0\Omega = 0.01\,\text{eV}$ (at $\sigma_0 = 0.7 \times 10^8\,\text{Pa}$), $kT = 0.025\,\text{eV}$ at room temperature, $s = 0.3\,\text{nm}$, and $D = 10^{-8}$ cm^2/s (the self-grain-boundary diffusivity of Sn at room temperature), we obtain a growth rate of $0.1 \times 10^{-8}\,\text{cm/s}$. At this rate, we expect a whisker of 0.3 mm after one year, which agrees well with the observed result. Since we assume grain boundary diffusion, we note that there are only several grain boundaries connecting the base of a whisker to the rest of the

Sn matrix. Hence, in taking the total atomic flux which supplies the growth of a whisker to be $JAdt\Omega$, where $A = 2\pi as$, we have assumed that the flux goes to the entire peripheral of the whisker "$2\pi a$" but only for a step height of "s" for its growth. The value of b and σ_0 used in the above calculation were taken from Ref. 17). These values are different from what we found in Ref. 24), where the stress of about 10 MPa or 10^8 dyne/cm^2 and the diffusion distance is of several grains or about 0.02 mm. Using the latter values, the calculated growth rate is about the same.

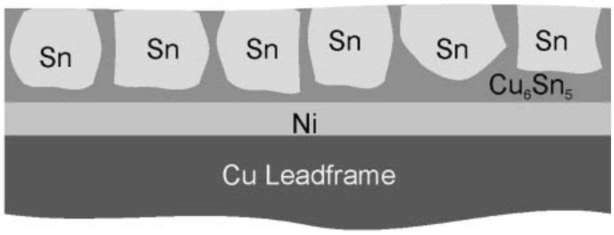

Fig. 12 A schematic diagram of the cross-section of a layer of Sn–2 to 5 mass%Cu finish plated on a Cu leadframe. The Sn grains in the finish are surrounded by grain boundary precipitates of Cu_6Sn_5.

5. Solutions to Prevent Sn Whisker Growth

On the basis of the above analysis, we have the three indispensable conditions of whisker growth; they are (1) The room temperature grain boundary diffusion of Sn in Sn, (2) The room temperature reaction between Sn and Cu to form Cu_6Sn_5, and it provides the compressive stress needed, and (3) The stable and protective surface Sn oxide. If we remove any one of them, we will have in principle no whisker growth. However, we found from the synchrotron radiation study that it takes only a very small stress level to grow a Sn whisker, hence it is difficult to prevent whisker growth. To remove the condition (3) is unrealistic since we have to have no oxide on the finish and to keep it in ultra-high vacuum.

At the moment, the industry solution or the solution recommended by National Electronics Manufacturing Initiative (NEMI) is to remove the condition (2) by preventing the Cu from reacting with Sn. The solution is to use matte Sn as the surface finish and to deposit a Ni layer on the Cu leadframe before the plating of the matte Sn.[3] The Ni diffusion barrier will prevent the diffusion of Cu into the matte Sn. Since most of the whiskers on matte Sn are short, they might not be a problem for devices that requires low reliability such as a cellular phone in consumer products. For low-end and low reliability electronic products, this low risk solution is being taken and the field data of failure in the next few yeas will verify whether the solution is good enough or not. Even if a few cellular phones may fail by whisker growth, it will not be a disaster. On the other hand, in military or aerospace industry, for example, where high reliability devices are required, the Ni/matte Sn solution is not good enough. This is because solder reacts with Ni and some Ni_3Sn_4 intermetallic compound can form within the matte Sn to generate a compressive stress.[30,31] Besides, one whisker is enough to fail a device.

To prevent Sn whisker growth, it is essential to uncouple the coupling between stress generation and stress relaxation. We must remove both stress generation and stress relaxation. Stress generation can be removed by blocking the diffusion of Cu into Sn with a diffusion barrier of Ni. However, up to now, no solution to remove stress relaxation is given. In other words, how to prevent the creep process or the diffusion of Sn atoms to the whiskers is unknown. To do so, another kind of diffusion barrier to stop the diffusion of Sn is needed. Since we have to block the grain boundary diffusion of Sn atoms from every grain of Sn in the finish, it is non-trivial. However, we can accomplish it by adding several percentage of Cu into the matte Sn or even the eutectic SnCu solder. We recall that the Cu concentration in the eutectic SnCu is only 1.3 at% or 0.7 mass%. We shall add about 2 to 7 mass% of Cu. We recall the cross-sectional microstructure of the eutectic SnCu in Fig. 4(a) shows that Cu_6Sn_5 will form as grain boundary precipitates. The reason to add so much of Cu is to have enough precipitation of Cu_6Sn_5 in all the grain boundaries in the Sn, so that every grain of Sn will be coated by a layer of Cu_6Sn_5. Thus, the grain boundary coating becomes a diffusion barrier to prevent the Sn atoms from leaving each of the Sn grains. When there is no diffusion of Sn, there is no growth of Sn whisker since the supply of Sn is cut. Figure 12 depicts a layer of Sn–2 to 7 mass%Cu finish on a Ni diffusion barrier on a Cu leadframe. There are grain boundary precipitates of Cu_6Sn_5 surrounding each grain of Sn, and the compound layer formed above the Ni could be $(Cu,Ni)_6Sn_5$.

There are two key reasons of the selection of Cu instead of other element to form grain boundary precipitate in Sn. The first is that when the Sn has so much supersaturated Cu, it will not be able to take more Cu from the leadframe. The second is that the adding of Cu will not affect much the wetting property of the surface of the finish. This is an important consideration since without a good wetting property, it cannot be used as finish on leadframes.

For low reliability devices, it will be sufficient to plate the Sn–2 to 5 mass%Cu directly on Cu leadframe without the Ni diffusion barrier. As it has been mentioned that when the Sn is supersaturated with Cu, it will not take more Cu from the leadframe. The advantage is that it is a low cost and simple process without the additional deposition of Ni. For high reliability devices, we shall keep the Ni diffusion barrier and deposit the Sn–2 to 7 mass%Cu finish on the Ni. In this combination, we have diffusion barriers to prevent the diffusion of both Cu and Sn. The combined solution will be much more effective than just using either one of them. What is the optimal concentration of Cu has to be determined. To plate the Sn 2 to 7 mass%Cu alloy is easier than the plating of eutectic SnCu which has only 0.7 mass%Cu. It is difficult to control the concentration within ± 1 mass% in electroplating. Cross-sectional SEM and focused ion beam images of the samples of electroplated Sn–2 to 7 mass%Cu should be obtained to investigate the microstructure, especially the distribution of grain boundary precipitates of Cu_6Sn_5 in Sn as a function of Cu.

The most important property of a surface finish is that it should be wetted easily by molten solder. The wetting behavior of eutectic SnPb on Cu_6Sn_5 and Cu_3Sn surfaces has been studied by using wetting balance tests.[32] While we expect the Sn–2 to 7 mass%Cu to be wetted by molten Pb-free solders, the wetting behavior and the effect of flux on wetting angle of molten eutectic SnAgCu solder on the plated Sn–2 to 7 mass%Cu surface has not been studied.

It is worth mentioning that because of the Ni barrier, we might consider to use Ni/Pd thin film finish instead of Pb-free solder finish to prevent Sn whisker growth. However, the mechanical properties of solder joints on Ni/Pd finish should be studied.[33,34)]

6. Summary

Spontaneous whisker growth on Sn surfaces is a surface relief phenomenon. Because it is spontaneous, the driving force must come from within the system and must be self-sustained in order to maintain the constant growth of whiskers. The driving force is a compressive stress coming from the chemical reaction between Cu and Sn and the stress is relaxed by whisker growth. To understand the mechanism of Sn whisker growth, we have to consider both stress generation and stress relaxation and their coupling by an irreversible process. As the compressive stress in Sn builds up due to the growth of Cu_6Sn_5 within the Sn, the surface oxide on the Sn is under tension and it will crack. The free surface area of the crack serves as source of vacancies, and the in-flux of vacancies will enable Sn atoms to diffuse out to reduce the compressive stress. Whiskers are eruptions on the oxide surface and become stress relief centers. The necessary and sufficient conditions of whisker growth are (1) The room temperature grain boundary diffusion of Sn in Sn, (2) The room temperature diffusion of Cu into Sn to form Cu_6Sn_5 in the Sn, and (3) The stable and protective surface Sn oxide. If we remove these conditions, we will have no whisker growth. NEMI has recommended a solution to remove the condition (2) by using a diffusion barrier to prevent the Cu from diffusing into Sn. We propose here to remove the condition (1) by blocking the grain boundary diffusion of Sn. A combination of these two solutions together is even better.

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