JOURNAL OF APPLIED PHYSICS VOLUME 92, NUMBER 1 1 JULY 2002

Tin whiskers studied by focused ion beam imaging and transmission electron microscopy

George T. T. Sheng and C. F. Hu
Macronix International Company, Hsinchu, Taiwan, Republic of China

W. J. Choi and K. N. Tu
Department of Materials Science and Engineering, University of California, Los Angeles, Los Angeles, California 90095-1595

Y. Y. Bong and Luu Nguyen
National Semiconductor Corporation, Santa Clara, California 95051

(Received 15 February 2002; accepted for publication 2 April 2002)

In surface mount technology of electronic packaging, the lead frames are finished with a layer of Pb-free solder. A large number of Sn whiskers are found on the surface of the finish, especially that of eutectic SnCu or pure Sn. The whiskers have a faster growth rate on an eutectic SnCu finish than on a pure Sn finish. Some of the whiskers on SnCu are long enough to short neighboring legs of the lead frame. We report here the study of spontaneous growth of Sn whiskers on these finishes using focused ion beam imaging and transmission electron microscopy. Cross-sectional samples, both normal and parallel to the growth direction of a whisker, were prepared. Precipitates of Cu_6Sn_5 in the grain boundaries of the finishes have been found. The growth of these grain boundary precipitates, due to the chemical reaction between Cu and Sn at room temperature, provides the driving force for spontaneous Sn whisker growth. Many more of these grain boundary precipitates exist in the SnCu finish than in the pure Sn finish. This is the main reason why Sn whiskers grow faster on the SnCu finish. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1481202]

I. INTRODUCTION

The tin (Sn) whisker is a well-known case of a surface relief phenomenon.[1–10] Currently there is renewed interest in Sn whisker growth due to the application of Pb-free solder in electronic manufacturing.[11,12] The Cu lead frame, which is used to package a chip to a printed circuit board, is electroplated or finished with a layer of Pb-free solder. Figure 1 depicts the cross section of a leg of a lead frame solder bonded to a board. The Si chip, which is not shown in Fig. 1, is wire bonded to the other end of the leg. The finish passivates the lead frame surface as well as enhances the wetting reaction during mounting of the legs onto the board. The Pb-free solder finish is typically eutectic SnCu or pure Sn. On the surface of the finish, especially of the eutectic SnCu, many long whiskers of Sn have been found. They are long enough, over 0.3 mm, to short two neighboring legs of the lead frame. The whiskers grow spontaneously during room temperature storage of the packaging and the growth rate is so fast that it takes only several weeks to reach a length that can bridge a pair of neighboring legs. Why Sn whiskers grow so fast on an eutectic SnCu surface, what the driving force is, and what the microstructure of grains surrounding the root of a whisker is are key questions that demand a systematic study.

We have used a focused ion beam (FIB) to prepare cross sections of the root of whiskers to obtain structural and morphological information on the Sn whiskers and the grains in the matrix surrounding them. We have also used the FIB to sputter away the surface oxide on the finish in order to examine the microstructure beneath the oxide. In addition, we have studied the microstructure of whiskers with conventional transmission electron microscopy (TEM). We observed many more precipitates of Cu_6Sn_5 in grain boundaries of the eutectic SnCu finish than in the pure Sn. The growth of these precipitates at room temperature provides the driving force of spontaneous whisker growth. The existence of a large number of these precipitates in the grain boundaries of SnCu is the reason why whisker growth is faster on the SnCu finish than on the pure Sn finish.

II. EXPERIMENT

A. Cross-sectional TEM samples prepared by FIB

Figure 2 shows a FIB image of the surface of the eutectic SnCu finish with two rectangular holes etched into the SnCu by ion beam etching. A thin piece of SnCu is left standing between the two holes. Before the FIB etching, a protective coating of a thin stripe of Pt was deposited onto the finish to protect the thin slice below the stripe from etching by the ion beam. This thin slice was prepared for TEM and it can be cut off and taken out. The inset at the upper-left corner in Fig. 2 shows a low magnification optical image of such a slice. The dimensions of this thin slice are about $25\ \mu m \times 25\ \mu m \times 100$ nm. Starting from the bottom side of the slice and going upward, we can recognize a layer of the Cu which is part of the core of the lead frame, a layer of intermetallic compound, a layer of the SnCu finish, and a whisker which is buried in the protective coating. In Fig. 2, we can see that there are several Sn whiskers in the vicinity of the two holes. Actually there was a short whisker between

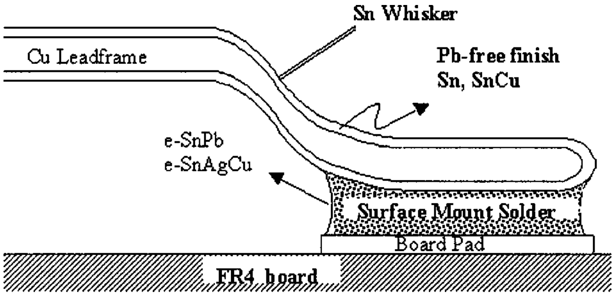

FIG. 1. Schematic diagram of the cross section of a lead frame leg mounted on a board.

the two holes before the FIB etching. The thin slice enables us to study the image of a cross section parallel to the growth direction of a whisker. This image also allows us to examine the grains surrounding the root of a whisker.

B. Cross-sectional samples prepared by FIB

The cross section polished by FIB is very smooth. It enables us to obtain a clear FIB image of the in-depth (normal to the surface of the finish) microstructures of grains, grain boundaries, and grain boundary precipitates in the finish, and the interface between the finish and the Cu. To begin with, we cut a cross section from a leg and polished it mechanically until it is close to a whisker. Then we used FIB etching to approach the whisker by continuously polishing an area about 25 μm$\times$25 μm until it reached the whisker. It made an indentation into the sample. Such a sample is shown in Fig. 3. The indented surface is cleaner than the mechanically polished surface which has much embedded debris. The indented surface can be analyzed by other surface techniques, such as microdiffraction, to determine the in-depth microstructure of the finish. The thickness of the finish is about 15 μm.

FIG. 2. Preparation of a thin slice sample by FIB for TEM study. Etching of two rectangular holes on the surface of the eutectic SnCu finish with a thin slice standing in between the two holes. A low magnification optical image of the slice is shown at the upper-left corner, from which we can see the Cu, the Cu–Sn compound layer, the SnCu finish, a whisker, and the protective coating.

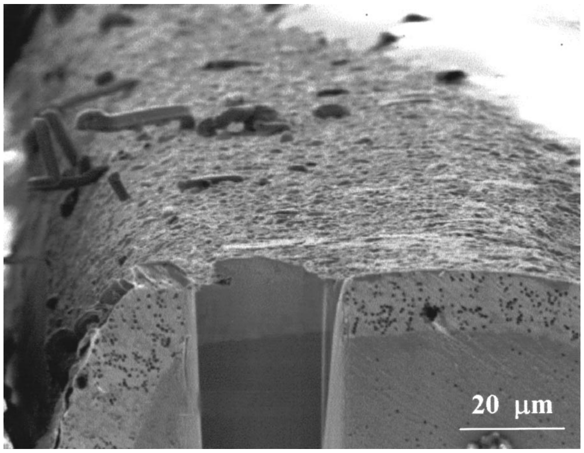

FIG. 3. SEM image of an indentation prepared by FIB etching. The image shows the cross section of a lead frame with the CuSn finish. The thickness of the finish is about 15 μm.

C. Conventional cross-sectional TEM samples

To obtain cross-sectional images of a whisker normal to its growth direction, we have used the conventional method to prepare TEM samples by sectioning and ion beam milling. Figures 4(b) and 4(a) show, respectively, the electron diffrac-

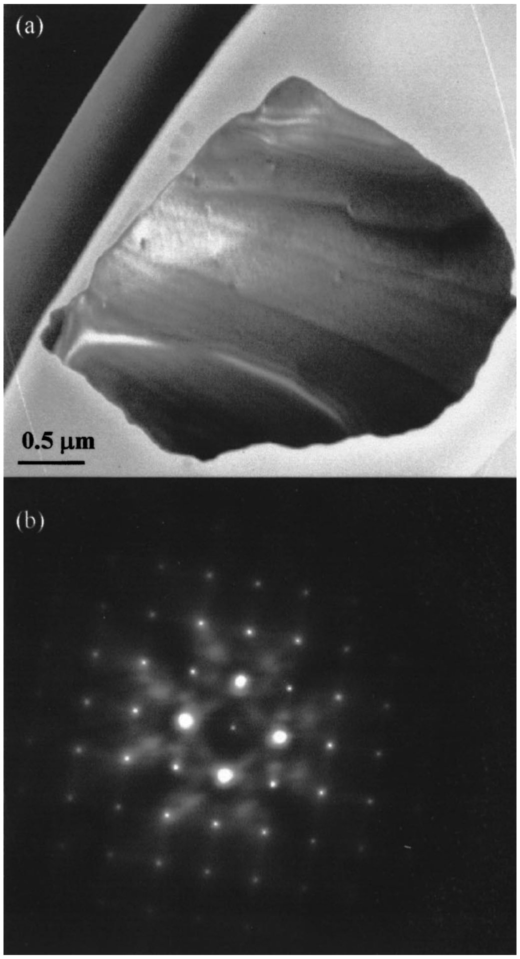

FIG. 4. (a) Cross-sectional TEM image of a whisker taken in the direction normal to its growth direction. (b) The corresponding [001] electron diffraction pattern of Sn.

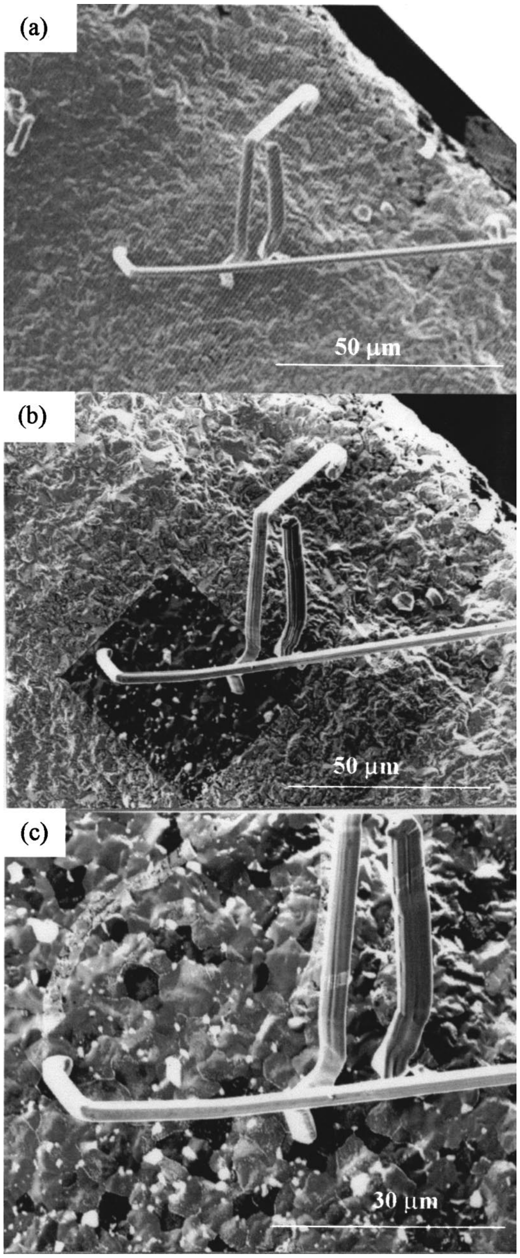

FIG. 5. (a) FIB image of a set of long whiskers on the surface of eutectic SnCu. (b) FIB image of the same area shown in (a) with a rectangular area sputtered clean of surface oxide. The sputtered area appears darker than the surrounding area. Many bright particles of Cu_6Sn_5 can be seen. (c) An enlarged FIB image of the microstructure in the sputtered area. The grain structure in the Sn matrix is clear and the Cu_6Sn_5 particles are located in the grain boundaries.

tion pattern and the corresponding transmission electron microscopic image of the cross section of a whisker. The growth direction of the whisker is [001]. There are a few dots in the image; they could be dislocations.

III. RESULTS

A. Whiskers on the surface of the eutectic SnCu finish

In Fig. 5(a), a FIB image of a group of whiskers on the SnCu finish is shown. Most of the whiskers in Fig. 5(a) are straight but some are bent at sharp angles. In Fig. 5(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. The thickness of the oxide was not measured. The sputtered area appears darker than the surrounding unsputtered area. The contrast depends on the degree of channeling of the ions; it appears dark when there is a high degree of channeling and it appears bright when there are more backscattered ions. Many bright images of particles of Cu_6Sn_5 are observed.

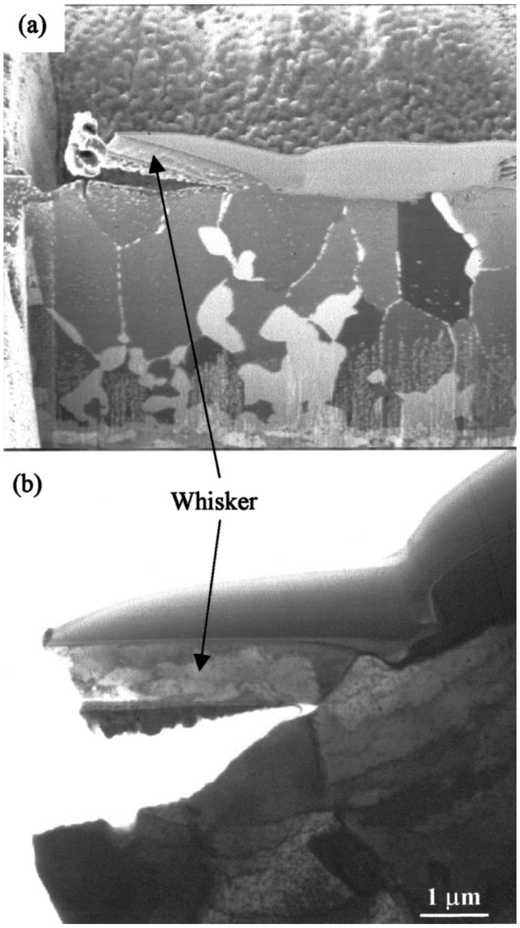

FIG. 6. (a) FIB image of a thin slice of the eutectic SnCu finish prepared by FIB thinning. The whisker is indicated by an arrow. Many grain boundary precipitates can be seen and they have been identified as Cu_6Sn_5 by elemental analysis. (b) Corresponding TEM image. The whisker is indicated by an arrow. While the whisker is a single crystal of Sn, it nevertheless contains a lot of defects and most of them are dislocations.

In Fig. 5(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 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 channeling. The diameter of the whiskers is about a few microns. It is the same as or comparable to the grain size in the SnCu finish. By combining Figs. 5(a) and 5(b), we conclude that some of the Cu_6Sn_5 precipitates have reached the interface between the SnCu and its surface oxide.

In Figs. 6(a) and 6(b), a pair of images shows, respectively, corresponding images of FIB and TEM of a thin slice,

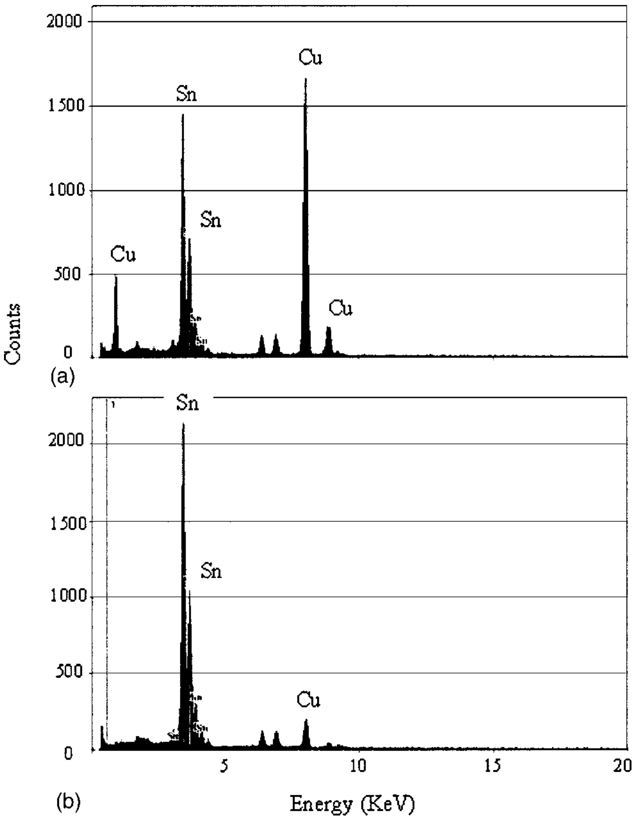

FIG. 7. (a) Elemental analysis of the grain boundary precipitate of Cu_6Sn_5. (b) Elemental analysis of a grain in the Sn matrix next to the Cu_6Sn_5.

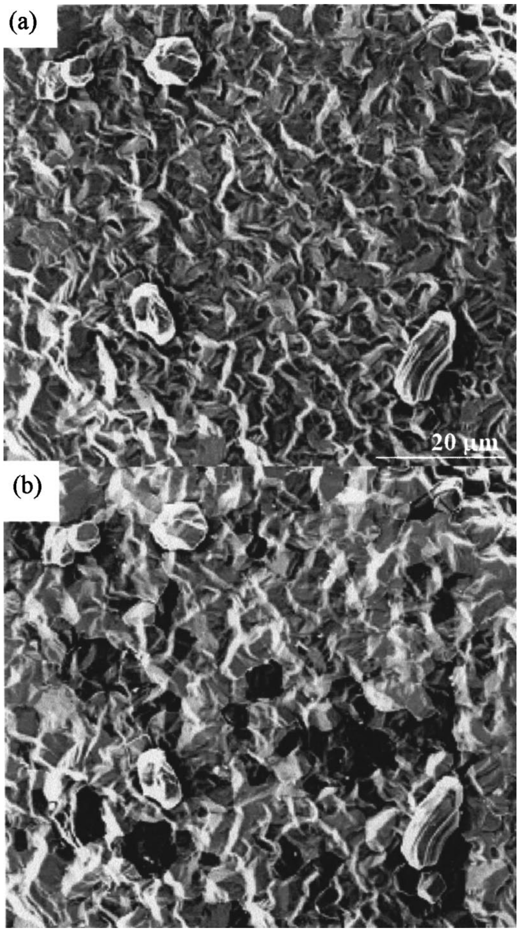

FIG. 9. (a) FIB images of short whiskers on the pure Sn surface. (b) FIB image of the same area shown in (a) after sputtering away the surface oxide. The grain structure in the Sn can be seen. However, very few Cu_6Sn_5 particles can be observed on the sputtered surface.

which is similar to the one shown in Fig. 2. In the cross-sectional FIB image in Fig. 6(a), we can see a crack in the upper left part of the image. The same crack can also be found in the upper left part in the cross-sectional TEM image in Fig. 6(b). The top layer above the crack is the protective layer needed to prevent etching of the thin slice by focused ion beam thinning. The image of the whisker which is below the top layer is indicated by an arrow in Figs. 6(a) and 6(b). While the whisker is a single crystal, it nevertheless contains observable defects. It is most likely that during focused ion beam preparation and thinning of the slice, the whisker was damaged and defects were introduced. The width of the whisker is about 1 μm. It may not represent the actual diameter of the whisker since the position of the thin slice may be away from where the diameter is. All the grains below the whisker are Sn grains. However, the interesting finding here is that there are many small precipitates of Cu_6Sn_5 in the grain boundaries in Sn, as can be seen in Fig. 6(a). They appear bright and the composition of these precipitates has been confirmed by elemental analysis to be Cu_6Sn_5, as shown in Fig. 7(a). Elemental analysis of the grain neighboring the precipitate has been found to be Sn, as shown in Fig. 7(b). The finding of these Cu_6Sn_5 precipitates enables us to understand both the origin of the compressive stress needed to drive whisker growth and why the eutectic SnCu finish has faster whisker growth than the pure Sn finish; this will be discussed in Sec. III B.

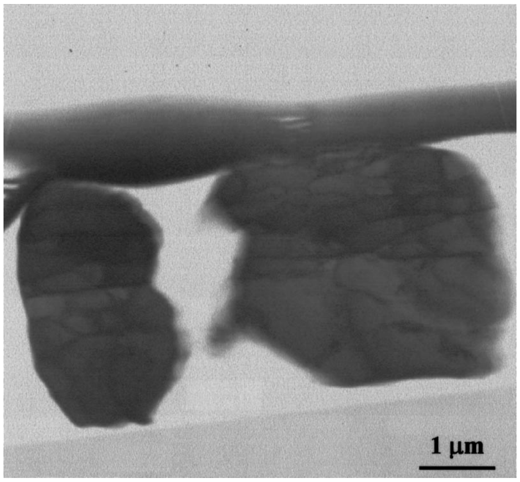

FIG. 8. Cross-sectional TEM images of a bent whisker on the eutectic SnCu finish. The images were taken from cross sections above and below the bend. There are many dislocations in the images.

A cross-sectional TEM image of a whisker normal to its growth direction was shown in Fig. 4. The cross-sectional images of a bent whisker, above and below the bend, are shown in Fig. 8. They contain a lot of dislocation networks. The corresponding selected area diffraction pattern (not

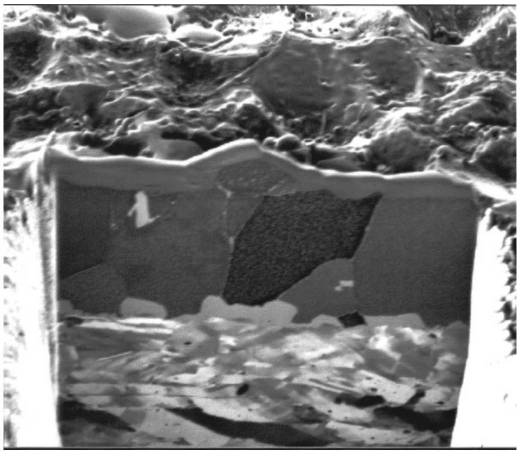

FIG. 10. FIB image of a cross-sectional area of the pure Sn finish prepared by FIB thinning. Very few grain boundary precipitates of Cu_6Sn_5 can be observed.

shown) showed that the growth direction of the whisker is [001].

B. Whiskers on the surface of the pure Sn finish

A FIB image of short whiskers on the pure Sn finish surface is shown in Fig. 9(a). Clearly, the morphology of the whiskers on SnCu and on pure Sn is different, shown, respectively, in Figs. 5(a) and 9(a). Besides the morphology, the rate of growth is much slower on the pure Sn finish. Figure 9(b) shows a FIB image of the same surface area of the pure Sn finish shown in Fig. 9(a) after the surface oxide was removed by ion beam sputtering. The grain structure in the Sn finish can be seen. Again we found that the size of the whisker is the same as or comparable to the grain size of the Sn. However, many fewer Cu_6Sn_5 precipitates are found in Fig. 9(b) as compared to in Fig. 5(b) or 5(c).

An image of the cross-sectional microstructure of pure Sn prepared by FIB is shown in Fig. 10. The region at the bottom is Cu, and above the Cu, there are a few bright Cu_6Sn_5 particles. The darker grains about the Cu_6Sn_5 are the Sn matrix. We find very few grain boundary precipitates of Cu_6Sn_5 in the Sn matrix. This is the major difference in microstructure between the eutectic SnCu finish and the pure Sn finish.

IV. DISCUSSION

We address two questions in the following. What is the driving force of spontaneous Sn whisker growth at room temperature? Why do whiskers grow faster on the SnCu surface than on the pure Sn surface?

It is known that Cu and Sn react at room temperature to form a Cu_6Sn_5 intermetallic compound.[13–15] The chemical energy per atom to form the compound is about 0.5 eV/atom, which is four to five orders of magnitude larger than the strain energy per atom at the elastic limit of Sn, about 10^{-5} eV/atom. It is known that in a diffusion couple where the dimension of the interface is much larger than the thickness, interdiffusion and reaction can cause bending of the couple. The diffusion of Cu into Sn to grow the Cu_6Sn_5 along the grain boundaries of Sn increases the volume and produces long range compressive stress in the neighboring grains.[16,17] To relieve compressive stress, layers of atoms normal to the stress direction must be removed and these atoms are driven by the stress gradient and diffuse to a whisker. The whisker itself is stress free. Since room temperature is a relatively high temperature for Sn, which melts at 232 °C, the self-grain boundary diffusion of Sn at room temperature is fast enough for stress relief. Similarly, the room temperature diffusion of Cu in Sn grain boundaries is also fast enough for the reaction to continue to grow the compound. Besides, the interstitial diffusion of Cu in solid Sn is extremely fast too; it is faster than 10^{-10} cm^2/s at room temperature. The continuous growth of the compound at room temperature will maintain compressive stress in the Sn matrix. Hence, Sn whisker growth on the Cu lead frame is a spontaneous phenomenon.

Most of the observed grain boundary Cu_6Sn_5 precipitates should have formed during the electroplating and aging at room temperature of the eutectic SnCu finish. Even if the SnCu finish has experienced reflow, most grain boundary precipitation of Cu_6Sn_5 should have occurred during solidification. In the molten state, the 0.7 wt % (or 1.3 at. %) Cu is in solution with Sn. In solidification, the Cu becomes supersaturated and precipitates out, so the microstructure is a matrix of basically pure Sn grains with Cu_6Sn_5 particles in the grain boundaries. Since the grain size in the Sn matrix is about several microns, it takes less than 1 s for Cu in the interior of a grain to diffuse to the surrounding grain boundaries and form Cu_6Sn_5. This is also true during electroplating of the finish. If some of the supersaturated Cu remains within the bulk of the Sn after plating, they should be able to diffuse to the grain boundaries during room temperature aging in a very short time. Why Cu_6Sn_5 prefers to form in grain boundaries rather than in the interior of grains may be a consequence of heterogeneous nucleation rather than homogeneous nucleation.

Whether the diffusion of the supersaturated Cu atoms in the bulk to the grain boundaries to form Cu_6Sn_5 would induce compressive stress in the Sn matrix or not is unclear. This is because it will depend on the difference in partial molar volume of Cu in the bulk of Sn to that in the Cu_6Sn_5. If it does, it is one of the reasons why eutectic SnCu enhances Sn whisker growth.

The Cu_6Sn_5 appears as random particles rather than a wedge or a thin and uniform layer in the grain boundaries of SnCu. In room temperature aging, these Cu_6Sn_5 particles in the grain boundaries may undergo ripening. In a closed system, where there is no more Cu coming from outside, it is constant volume ripening and most likely the ripening will not generate compressive stress in the surrounding Sn matrix. On the other hand, what we have here is an open system: during room temperature aging the Cu atoms from the lead frame diffuse along grain boundaries and grow more and/or larger Cu_6Sn_5 in the grain boundaries of the finish. Or, the Cu atoms may reach the grain boundary precipitates via interstitial diffusion in the SnCu (or pure Sn) finish. The morphology of these Cu_6Sn_5 particles suggests that the compressive stress and stress gradient generated by their growth will be nonuniform. Due to the fact that the distribution of these grain boundary precipitates may be random, the stress distribution may be random as well. In the region where the density of grain boundary precipitation is high, the compressive stress will be high too. It could be the region wherein a whisker nucleates more easily. The pre-existence of many Cu_6Sn_5 particles in the SnCu finish, compared to many fewer Cu_6Sn_5 particles in the pure Sn finish, is the main reason why Sn whisker growth is faster on the SnCu finish. Without pre-existing Cu_6Sn_5 particles in the pure Sn finish, Cu atoms must penetrate and be accompanied by intermetallic compound (IMC) formation in the grain boundaries of Sn, a wedge shape of IMC is expected[17] and the rate of penetration has been calculated to have a $t^{1/4}$ dependence.[18,19]

While compressive stress is a necessary condition for whisker growth, it is insufficient. The other necessary condition is a protective surface oxide on the sample surface and the whisker surface.[16,20] The growth of whiskers requires long range grain boundary diffusion of Sn atoms. With a protective oxide on the surface as shown in Fig. 5(b), the surface is not an effective source or sink of vacancies. No stress relaxation can occur locally by Nabarro–Herring creep or Coble creep.[21] The pre-existence of grain boundary Cu_6Sn_5 particles may have enhanced the long range diffusion of Sn along the grain boundaries. This is because, while the growth of a grain boundary particle tends to exert compressive stress on the grains on its two sides, it nevertheless exerts tensile stress and opens up the grain boundary between the grains. The oxide on the whisker surface is needed to prevent lateral growth in order to maintain a constant cross section of the whisker.

The grain boundaries between the whisker and neighboring grains are of keen interest since on the whisker side it should have no strain or much less strain than on the other side. A stress or strain gradient is expected. It is also the interface (grain boundary) of growth of the whisker. However, the image shown in Fig. 6(b) does not have the resolution to reveal the change in atomic structure across the interfaces (grain boundaries) because of ion beam damage. Hence, better sample preparation and higher resolution TEM images of these grain boundaries would be desirable.

The eutectic SnCu contains 0.7 wt. % (or 1.3 at. %) of Cu. In electroplating, it is hard to control such a low concentration of Cu precisely. If there is more Cu in the finish, the precipitation of Cu_6Sn_5 will be greater and whisker growth will be faster. On the other hand, a lesser amount of Cu may reduce whisker growth, but the solder will consume more Cu from the under-bump metallization or the bond pad.

V. SUMMARY

We have studied the surface morphology and cross-sectional microstructure of a Sn whisker on a Pb-free solder finish using focused ion beam imaging and transmission electron microscopy. On the eutectic SnCu surface, Sn whiskers are much longer than those on the pure Sn surface. There were many Cu_6Sn_5 precipitates on the surface of the SnCu finish when the surface oxide was sputtered away, and the precipitates appear along the grain boundaries of SnCu. Similarly, in the cross section parallel to the growth direction of whiskers, we found many more Cu_6Sn_5 precipitates in the grain boundaries of the eutectic SnCu than in the pure Sn. The growth of these grain boundary precipitates at room temperature provides the driving force for spontaneous Sn whisker growth. The pre-existence of these grain boundary precipitates in eutectic SnCu is the reason why whiskers grow faster on the eutectic SnCu finish than on the pure Sn finish. In the cross section normal to the growth direction of the whiskers, the whiskers were found to be single crystal. Most of them grow along the [001] direction.

ACKNOWLEDGMENT

The authors at UCLA would like to acknowledge support by SRC/NSC Contract No. NJ-853.

[1] C. Herring and J. K. Galt, Phys. Rev. **85**, 1060 (1952).
[2] G. W. Sears, Acta Metall. **3**, 367 (1955).
[3] A. P. Levitt, in *Whisker Technology* (Wiley–Interscience, New York, 1970).
[4] U. Lindborg, Metall. Trans. A **6A**, 1581 (1975).
[5] T. Nagai, K. Natori, and T. Furusawa, J. Jpn. Inst. Met. **53**, 303 (1989).
[6] I. A. Blech, P. M. Petroff, K. L. Tai, and V. Kumar, J. Cryst. Growth **32**, 161 (1975).
[7] N. Furuta and K. Hamamura, Jpn. J. Appl. Phys. **8**, 1404 (1969).
[8] W. C. Ellis, D. F. Gibbons, and R. C. Treuting, in *Growth and Perfection of Crystals*, edited by R. H. Doremus, B. W. Roberts, and D. Turnbull (Wiley, New York, 1958), p. 102.
[9] R. Kawanaka, K. Fujiwara, S. Nango, and T. Hasegawa, Jpn. J. Appl. Phys., Part 1 **22**, 917 (1983).
[10] U. Lindborg, Acta Metall. **24**, 181 (1976).
[11] Y. Zhang, C. Xu, C. Fan, and J. A. Abys, J. Surf. Mount Technol. **10**, 17 (2000).
[12] R. Schetty, Circuit World **27**, 17 (2001).
[13] K. N. Tu, Acta Metall. **21**, 347 (1973).
[14] J. W. Mayer, J. M. Poate, and K. N. Tu, Science **190**, 228 (1975).
[15] K. N. Tu and R. D. Thompson, Acta Metall. **30**, 947 (1982).
[16] K. N. Tu, Phys. Rev. B **49**, 2030 (1994).
[17] B. Z. Lee and D. N. Lee, Acta Mater. **46**, 3701 (1998).
[18] J. C. Fisher, J. Appl. Phys. **22**, 74 (1951).
[19] P. G. Kim, J. W. Jang, K. N. Tu, and D. Frear, J. Appl. Phys. **86**, 1266 (1999).
[20] C. Y. Chang and R. W. Vook, Thin Solid Films **228**, 205 (1993).
[21] C. Herring, J. Appl. Phys. **21**, 437 (1950).