Transmission Electron Microscopy of Spontaneous Tin (Sn) Whisker Growth under High Temperature/Humidity Storage

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Abstract

The present work is devoted to characterize the microstructures of Sn/Cu lead-frame attached on the printed circuit board (PCB) and of tin-whiskers formed on the Sn-surface after exposure under 85°C/85 %RH for 1000 and 2000 h in order to verify the whisker-growth behavior. Whiskers were observed on the un-corroded and corroded Sn-surfaces and confirmed to be of Sn β–phase. The number of whiskers was relatively small. Within the corroded area Sn was oxidized to be SnO_2. The SnO_2 domain is made of nanocrystalline grains about 10-20 nm in size for specimen exposed for 1000 h, whereas in another one exposed for 2000 h an amorphous phase is included in the SnO_2 domain. Intermetallic compound (IMC) of Cu_3Sn and Cu_6Sn_5 is formed at the Sn/Cu interface. The results suggest that there is competitive stress generation according to formation of the Cu-Sn IMC and the Sn-oxide phase during oxidation and corrosion process. The stress-driven diffusion of Sn-atoms from the higher-stress area into the lower-stress area to form whiskers is discussed.

Keywords: Sn/Cu lead-frame, oxidation, tin-whisker, microstructure, TEM

Introduction

It is well known that tin whiskers growing on the surface of Sn-based plating alloys especially filament-type whiskers can cause a serious problem in creating electrical shorts in electrical and electronic assemblies during device operation. It is also well known that the compressive stress within the electroplated Sn one of fundamental causes of whisker formation. It was reported that the compressive stress can be generated by many factors such as internal stresses [1-3], the Sn-oxide film [4], electrical currents [5] and surface corrosion due to high humidity [6-8]. Besides, many researchers [9-11] have reported that the intermetallic compound (IMC) of the Cu-Sn phase dominantly generates the compressive stress and drive the whisker formation.

Recently, some research groups have been extensively investigated whisker formation and growth on the corroded Sn-surface corrosion due to high humidity storage [6-8, 12]. Osenbach *et al* [6] has studied whisker formation on the Sn plated Cu and Ni/Cu that were exposed to condensing and noncondensing environments under 60°C/93%RH for various durations. They indicated that whisker formation and growth are faster in condensing environments comparing with that in non-condensing ones. Oberndoff *et al* [7] has confirmed that condensation accelerates whisker growth regardless the kind of lead-frame material. They have reported that whiskers started to grow after 2000 h at 60°C/93%RH. Moreover, characterization of whisker growth including growth rate under the condition of 60°C/93%RH and 85°C/85%RH storage has been studied by Nakadaira *et al* [8]. They implied that the growth of whiskers and spread of corrosion are much faster at 85°C/85%RH than at 60°C/93%RH.

According to their discussions, Nakadaira *et al* [8] has stated that molar volume of the Sn-oxide is larger than that of β-Sn, providing large compressive stress within the Sn-film induced by corrosion. This statement is consistent with that of Oberndoff *et al* [7]. Inversely, Osenbach *et al* [12] has found that molar volume of the Sn-oxide is smaller than that of Sn, leading localized oxidation in and around the Sn-oxide/Sn interface. Accordingly, the effect of oxidation in whisker formation is smaller than that of the Cu-Sn IMC.

When Sn plated Cu is exposed to high temperature and high humidity, oxidation and corrosion will occur. There would be at least two possible sources of compressive stress generation: from the Sn-oxide layer on the Sn-surface and the Sn-layer, and the Cu-Sn IMC at the Sn/Cu interface. However, which stress will dominantly contribute to drive the whisker formation has not been fully understood. The exact mechanism of the whisker growth due to surface corrosion, therefore, is still opened for discussion. In this report we characterized the microstructures of Sn/Cu lead-frame attached on the printed circuit board (PCB) with tin whiskers formed after exposure to high temperature/humidity environment in order to verify the whisker-growth behavior under this condition.

Experimental

The tin layer about 10 μm in thickness was electroplated on a Cu substrate to be an electric terminal on the PCB, then exposed to 85°C/85 %RH for 1000 h and 2000 h. Cross-section thin foil specimens for transmission electron microscopy (TEM) were prepared by a focused ion beam (FIB) equipped with a microsampling unit. FIB (FB-2000K, Hitachi) with Ga^+ used for milling and was operated at accelerating voltage of 30 kV. The specimen surface was coated with carbon (C) and tungsten (W) before preparing the microsamples. The microsample was tightly attached on the molybdenum (Mo) mesh-holder. In the case of tin specimen, selection of mesh material should be considered to avoid the side effect of reaction between Sn and mesh material due to Ga^+ bombardment during FIB milling.

Microstructures were observed from plan- and cross-section-views with an optical microscope, a scanning electron microscope (SEM), a scanning ion microscope (SIM) coupled in FIB (FIB-SIM) and a TEM (Tecnai-F20, FEI) equipped

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with scanning-TEM and energy-dispersive-x-ray spectroscopy (STEM-EDXS).

Results and discussion

Specimen exposed to 85 °C/85 % RH for 1000 h

Typical specimen used in this study is represented in Figure 1. It displays about 20 pins of Sn plated Cu attached on the PCB after exposure to 85°C/85 % RH for 1000 h. Careful observation on the Sn-surface of each pin surface indicates

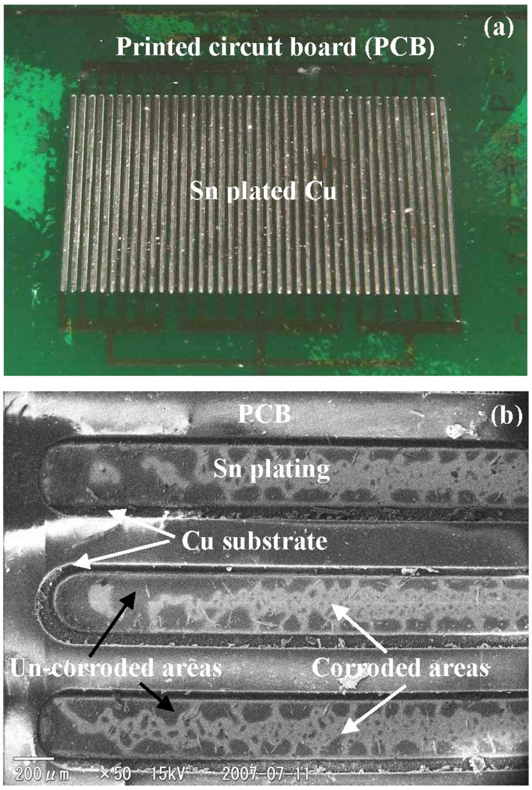

Fig. 1. (a) A digital camera photograph showing all pins of Sn plated Cu on PCB and (b) a SEM micrograph showing magnified pins with corroded and un-corroded areas indicated with white and black arrows, respectively.

that long whiskers and the shorter ones were observed on entire surface of pins. However, the number of whiskers is relatively smaller comparing with that of whiskers formed by other factors such as applied external stress and thermal cycle treatment [13, 14]. According to SEM micrograph depicted in fig. 1 (b), it is seen that Sn-surface was non-uniformly corroded. The formation of corroded areas appears as bright contrast where they are mainly concentrated as a continuous layer on the middle of the entire pin surfaces. The corrosion layer seems to form locally and become thinner toward the edge of pins. In this case, it has been found that whiskers are grown from both un-corroded and corroded Sn-surface as demonstrated in fig. 2 (a) and (b), respectively. Interestingly, on the un-corroded Sn-surface the whisker is kinky grown near the Sn-surface and surface of the whisker. To simplify the microstructure characterization according to the shape of this whisker we have designated it to be part I, II and III. It is also seen that cracking is formed near the whisker root (part I), interpreting this might be the path of oxygen atoms diffuse

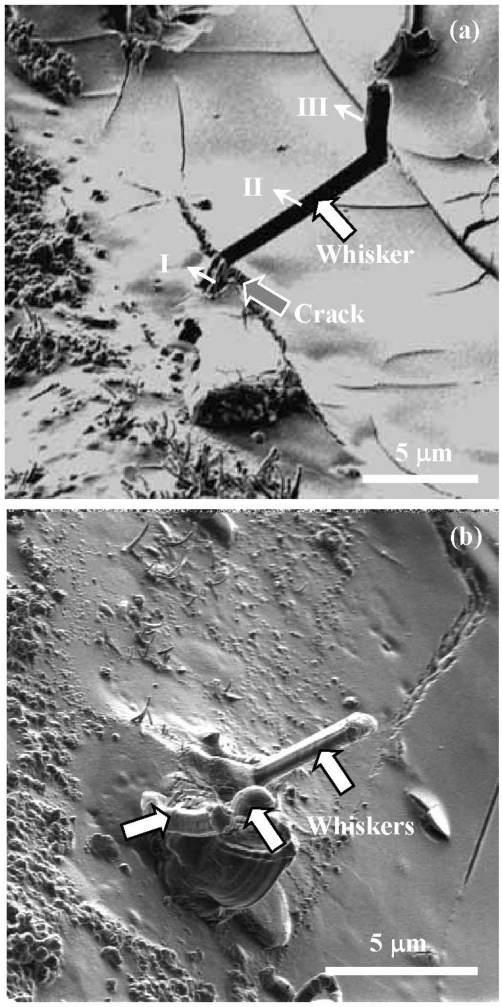

Fig. 2. FIB-SIM images of morphology of whiskers after specimen exposed to 85°C/85 % RH for 1000 h. (a) Whisker grown from the un-corroded Sn-surface and (b) whiskers grown from the corroded Sn-surface.

into the Sn-layer. Unlike another whisker which is grown from the corroded Sn-surface, there are several whiskers growing on the same place. A whisker grows straight and the other ones grow with irregular shape. In this study, we have characterized the microstructures of kinky and straight whiskers which are grown from un-corroded and corroded Sn-surfaces, respectively.

A cross-sectional bright field STEM (BF-STEM) image of the whisker grown on the un-corroded Sn-surface is depicted in fig. 3 (a). In this figure, it is shown carbon and tungsten that were deposited on the specimen surface before preparing the microsample. Holes formed on the Sn-surface are affected by Ga^+ bombardment during FIB milling. Besides, cracking formed near the whisker root shown in fig. 2 (a) is also recognized as marked by a thick black-arrow. In this specimen, Sn-layer was partly corroded at the grain and grain boundaries that appear as bright contrast with fine needle-like structure. The whisker seems to grow from the un-corroded Sn-grains. Careful observation of microstructures in the whisker body parts I and II (fig. 3 (b)) has confirmed some features as follows. In the part I, it is characterized that the whisker is standing on the two un-corroded Sn grains. No sub grains are found. While in the part II, a few numbers of dislocations are recognized. But, no direct evident for the presence of dislocations within the whisker related to the whisker formation in this specimen. Electron diffraction patterns (EDPs) displayed in fig. 3 (c) and (d) are obtained from the Sn-grain and the whisker body part I as encircled in (c') and (d'), respectively. Analysis of those indicates that both the Sn-grain and the whisker are of β-Sn phase. Then, analysis of an EDP (fig. 3 (e)) obtained from the corroded Sn-grain as encircled in (e') shows that tin was oxidized to be

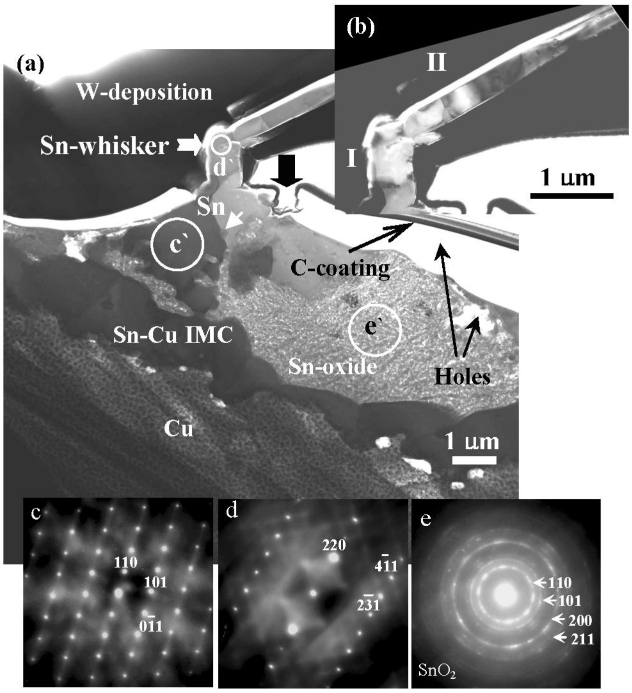

Fig. 3. (a) A cross-sectional BF-STEM image of tin-whisker growing on the un-corroded Sn-surface, (b) BF-TEM image of the whisker body, (c-e) electron diffraction patterns (EDPs) obtained from tin-grain (c`), whisker body (d`) and the Sn-oxide area (e`), respectively.

polycrystalline SnO_2. The region of SnO_2 is made of nanocrystalline grains about 10-20 nm in size as confirmed from high resolution TEM (HRTEM) image. Furthermore, STEM-EDXS analysis result recognized that the Sn-oxide layer of about 100 nm covered the un-corroded Sn-surface. Besides, intermetallic compound (IMC) of the Cu-Sn phase is formed at the Sn/Cu interface as a layer with inhomogeneous thickness about 500 nm to 2.5 μm. A small precipitate of the Cu-Sn phase is observed at the Sn-grain boundary as indicated by a small white-arrow. It is possibly resulting from diffusion of Cu-atoms into the Sn-layer through the Sn-grain boundary, it is not resulting from FIB milling as described by Osenbach *et al* [6].

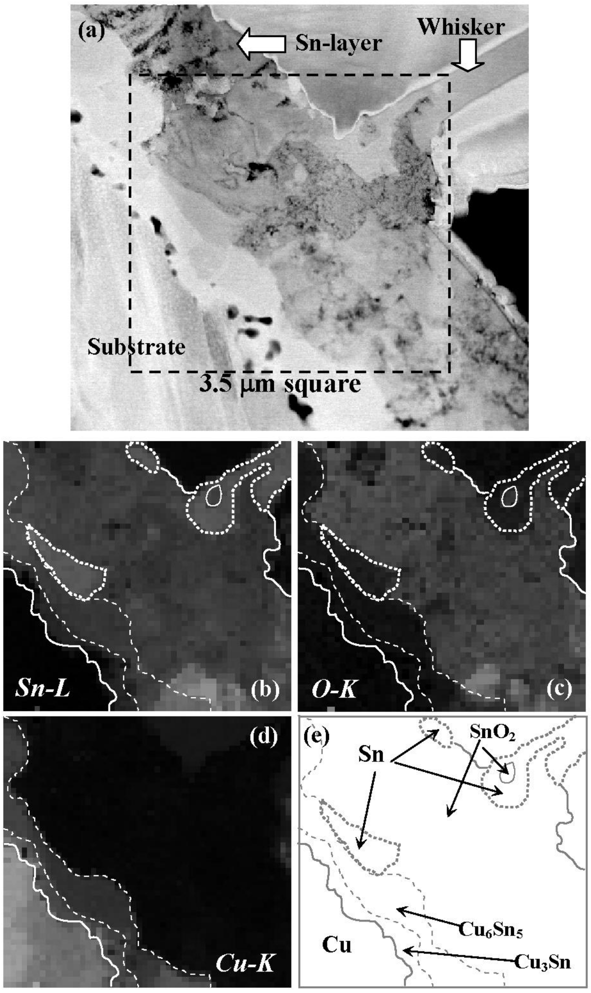

Fig. 4. Two-dimensional STEM-EDXS elemental mapping: (a) a cross-sectional BF-STEM image of tin-whisker growing on the corroded Sn-surface, (b) Sn-map, (c) O-map, (d) Cu-map and (e) schematic diagram of chemical compound distribution.

On the other hand, a whisker grown on the corroded Sn-surface is demonstrated in a cross-sectional BF-STEM image in fig. 4 (a). Figure 4 (b) – (d) reveal two-dimensional elemental mapping for Sn, O and Cu, respectively. It is clearly shown in fig. 4 (b) and (c) that the entire area within the Sn-layer has high concentration of tin and oxygen atoms. This leads that Sn-layer was almost completely oxidized to be polycrystalline SnO_2 as confirmed from EDPs analyses obtained from corroded areas. It is exhibited that small region within the Sn-layer remains un-corroded. Then, areas within the whisker body and a part of whisker root appear to be un-corroded. IMC layer of the Cu-Sn phase formed in this area is rather thinner compared with that in another one. The layer consists of Cu_3Sn and Cu_6Sn_5 that are formed on above the Cu substrate and above Cu_3Sn IMC, respectively as confirmed by EDXS profile analysis. The distribution of chemical compound within the elemental mapping area is summarized in fig. 4 (e). Cu atoms are almost not identified within the Sn-layer. As mentioned above that effect of FIB milling during thinning down the specimen is not resulting in the formation of thin-formation of the Cu-Sn IMC at the Sn-grain boundaries as stated in Ref. [6].

Specimen exposed to 85 ℃/85 % RH for 2000 h

After long storage for 2000 h, the microstructure differences in the Sn-layer and whisker formation have been observed. The Sn-layer was almost completely corroded. A part of Sn-layer was extremely corroded resulting in broken Sn-oxide as is shown in fig 5 (a). The whisker grown from the broken Sn-oxide is indicated in a circle closed-line. Another whisker that is marked in a circle dotted line is possibly a part of the whisker body separated from its original growth place.

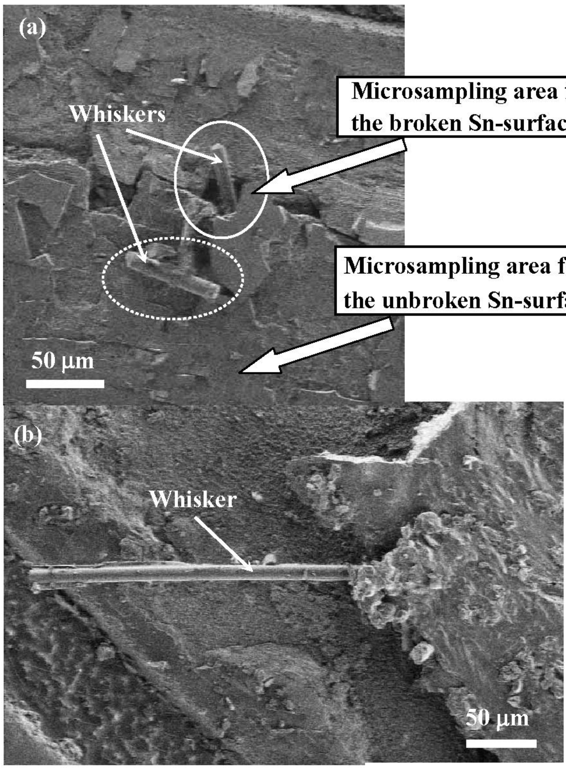

Fig. 5. FIB-SIM images of morphology of whiskers after specimen exposed to 85°C/85 % RH for 2000 h. (a) A whisker grown from the unbroken Sn-oxide and (b) the whisker grown from the broken Sn-oxide. The microsampling areas are shown.

Whiskers grown in this specimen are very small in number, but typically very large in size comparing with that grown on the specimen exposed for 1000 h. Fig 5 (b) demonstrates a whisker with size of about 200 µm in length and 15 µm in diameter that is strongly grown from the unbroken Sn-oxide. The size of whisker is too large to prepare thin foil specimen for TEM observation by a FIB microsampling technique. Although to prepare a cross-sectional specimen by FIB milling it was very difficult and time consuming. Therefore, microstructure examination on this specimen has not been focused on the whisker, but on the Sn-layer located on the broken Sn-oxide and on the un-broken Sn-oxide as shown in fig. 5 (a).

Microstructure of the broken Sn-oxide

Figure 6 (a) reveals a microstructure of the Sn-oxide film. This thin foil was obtained from the broken surface where Sn-layer was extremely corroded. This figure shows two areas: bright and dark areas with quite different microstructures. The presence of a hole in the bright area was formed during FIB milling. Actually, the microstructure as shown in fig. 6 (a) is our new finding in microstructure observation of the Sn-oxide film so far. Analyses of EDPs in fig 6 (b) – (g) obtained from the positions as encircled in (b') – (g') in the bright region and the dark region, respectively, imply that the entire area of the Sn - oxide is made of polycrystalline SnO_2 containing the

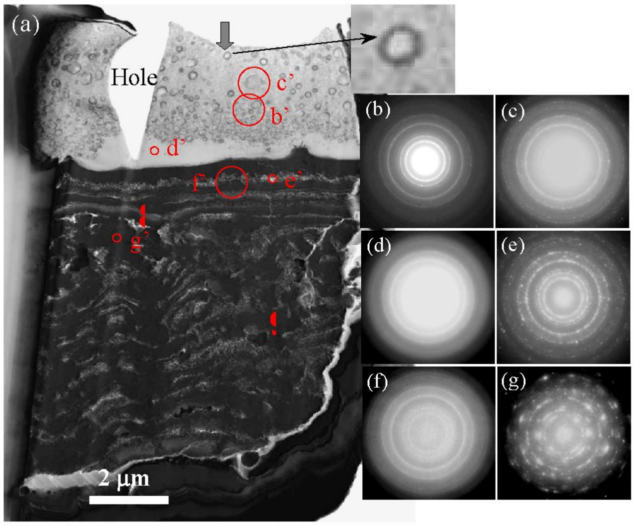

Fig. 6 (a) BF-STEM image of the Sn-oxide film obtained from the broken surface, (b, c, d, e, f and g) typical EDPs of SnO_2 obtained from the encircled areas in b', c', d', e', f' and g', respectively. Diffuse intensity in (c), (d) and (f) show the existence of amorphous phase.

amorphous oxide-phase. The bright region is featured by an amorphous layer of the Sn-oxide that is formed in the bottom as shown an EDP (fig 6 (d)) with strong diffuse intensity. Above the amorphous layer, the microstructure is characterized by a ring-like structure in which the small ones are densely distributed near the amorphous layer and the bigger ones are distributed with relatively low density toward the Sn-oxide surface. Careful observation on the bigger ring-like structure as depicted in the magnified image, it was shown that the circled dark ring is made of nanocrystalline grains with the size of about 10 nm. Interestingly, in the middle of the ring-like structure that appears as bright contrast was featured by amorphous phase as confirmed from a HRTEM image. Therefore, diffused intensity shown in an EDP (fig. 6 (b) and (c)) is coming from the amorphous phase formed in the middle of ring-like structure. Furthermore, in contrast to the bright area, the dark area is characterized by bright and dark layer-structures. Concerning the EDPs obtained from the bright and dark layers as exhibited in fig. 6 (e) and (g), respectively, no strong diffuse intensity is depicted. However, an EDP in fig 6 (f) happens to show slightly-strong diffuse intensity, explaining that the amorphous oxide-phase might be inhomogeneously distributed within the dark area.

Whisker formation and growth mechanism

In the present investigation, it is considered that the compressive stress would be generated from two sources: i.e. from the formation of the Cu-Sn IMC at the Sn/Cu interface and the Sn-oxide phase on the Sn-surface and within the Sn-layer. In this case, with regard to the statement indicated by Nakadaira *et al* [8] that the growth of whiskers is faster at 85°C/85%RH than at 60°C/93%RH. This explained that increase of the temperature would provide effect on the whisker growth stronger than increase of relative humidity. In fact, the whisker formation and growth resulting in this investigation cannot be directly compared with the results reported by Osenbach *et al* [6], Oberndorff *et al* [7] and Nakadaira *et al* [8], because of the difference in environment condition. They exposed their specimens to the condensing environment and, treatments of annealing and thermal cycle were also conducted after corrosion.

Based on the experimental results, it is interpreted that high temperature tends to accelerate the diffusion of Cu-atoms through the Sn/Cu interface and Sn-grain boundaries to form Cu_3Sn and Cu_6Sn_5 IMC. While high humidity tends to accelerate the diffusion of oxygen from the outermost Sn-surface into the Sn-layer to form the Sn-oxide phase on the Sn-surface and SnO_2 inside. Formation of the Cu-Sn IMC and the Sn-oxide phase may generate the compressive stress which drives the diffusion of Sn-atoms from high-stress region into the lower-stress region to form whiskers. However, in order to understand whether the Cu-Sn phase or the Sn-oxide phase will provide a dominant effect to the whisker formation, diffusion controlled for Cu-atoms into Sn-grains and oxygen-atoms into Sn-grains should be considered.

According to two whiskers formed on the specimen exposed for 1000 h where they obtained from the un-corroded and corroded areas, the mechanism of whisker formation and growth can be considered as follows. At the beginning of the oxidation and corrosion processes, there is competitive generation of compressive stress due to the Cu-Sn IMC and the Sn-oxide phase. At 85°C in the early state, the diffusion rate of Cu-atoms into the Sn-layer would be much more higher than that of oxygen atoms into the Sn-layer. For oxygen, in this case, tin and oxygen reacts to form the Sn-oxide layer on the Sn-surface, and this Sn-oxide layer will pin the diffusion of oxygen atoms into the Sn-layer. The accumulated stress within the Sn-oxide layer due to molar expansion of the Sn-oxide would be easy to break a thin Sn-oxide where an oxide layer is apt to be broken at the grain boundary. Thus, high humidity and increase of duration times will then accelerate the diffusion of oxygen atoms through the broken Sn-grain boundaries to form the corroded area both within the Sn-grains and Sn-grain boundaries. While the corrosion process is taking place, the stress generated by Cu-Sn IMC drives the diffusion of Sn-atoms from high-stress region into the lower-stress region to form whisker nuclei. High compression stress generated by the Cu-Sn IMC would become higher with increase of the corroded area within the Sn-layer. This will accelerate in driving the Sn-atoms diffuse into the stress-free region of the Sn-surface to form and grow whiskers and also into the whisker nuclei to grow whiskers. Local corroded area in this specimen may be resulting from inhomogeneous formation of the Sn-oxide layer on the Sn-surface. The exposure time larger than 1000 h under 85°C/85 %RH is though to be not effective to verify the mechanism of whisker formation.

Conclusions

The microstructure of the Sn/Cu lead frame with spontaneous tin whiskers growing after exposed to 85°C/85%RH for 1000 and 2000 h has been investigated using SEM, FIB-SIM, TEM and STEM-EDXS.

(1) Sn whiskers
   a) Whiskers grown on this specimen are relatively small in number especially after exposed for 2000 h. The whisker reached the size of about 200 μm in length and 15 μm in diameter after long storage for 2000 h.
   b) Whisker were grown from both the un-corroded Sn-surface and the corroded Sn-surface.

(2) The Cu-Sn IMC
   a) The Cu-Sn phase of Cu_3Sn and Cu_6Sn_5 IMC is formed at the Sn/Cu interface as a layer with inhomogeneous thickness about 500 nm to 2.5 μm.
   b) The presence of Cu-Sn phase at the Sn-grain boundary is almost not found.

(3) Sn-layer due to oxidation and corrosion processes
   (a) After specimen exposed for 1000 h, the Sn-layer was locally corroded at the Sn-grains and Sn-grain boundaries. Within the corroded area Sn was oxidized to be polycrystalline SnO_2 which is made of nanocrystalline grains about 10-20 nm in size. The Sn-oxide of about 100 nm in thickness is formed on the un-corroded Sn-surface.
   (b) After specimen exposed for 2000 h, the Sn-layer was completely and in a part extremely corroded. The corroded area consists of polycrystalline SnO_2 and the amorphous phase of Sn-oxide.

Based on the observation results we have pointed out that at the early state of oxidation and corrosion processes the stress generated from IMC will dominantly drive the diffusion of Sn-atoms from high-stress region into the lower-stress region to form whiskers. During the process, the accumulated stress within the Sn-oxide layer due to molar expansion of the Sn-oxide would break a thin Sn-oxide at the grain boundary. High humidity and long storage will accelerate the corrosion process within the Sn-layer which then increases the stress as driving force to form and grow whiskers.

Acknowledgments

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