Tin Whisker Formation on a Lead-free Solder Alloy Studied by Transmission Electron Microscopy

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Abstract

Tin whiskers grown on a Sn/Cu-plated Polyimide (PI)-flexible substrate are a serious problem in electronic industrial application, because the whiskers lead to catastrophic electrical short circuit failures. Here, we report characterization of microstructures in the whiskers grown on a surface of Sn/Cu-plated PI-flexible substrate by cross-sectional transmission electron microscopy (TEM) to analyze the behavior and the formation mechanism of whiskers. The whisker was found to be monocrystalline β-Sn and grown with the preferred directions of [110] and [101]. The whiskers formed on this tin surface are nucleated and grown by the compressive stress, that is induced externally by insertion of Sn/Cu-plated PI-flexible substrate into the connector.

Keywords: Tin whisker, Lead-free alloy, Microstructure, TEM

1. Introduction

The rapidly increasing market for electronic products implies the increase of requirements on the performance, reliability and cost of the electrical components, for instance, the connector. A connector is used to transfer signals from a conductor to another with no or limited distortion. Thus, the role of connector for electronic industrial application such as computer, telecommunication, aerospace and automotive industries is quite significant.

Nowadays, use of lead (Pb) – tin (Sn) plating alloys for the connector and flexible substrate is replaced by tin lead-free alloys due to high potential risk of Pb on the human body and environment. Polyimide is widely used for flexible substrate in electrical interconnecting application and for other advanced applications because it provides some good advantages in mechanical, electrical (high heat-resistant) and biological characteristics [1, 2]. Flexibility of polyimide is intended to provide strain relief against the force of micromotion in contact with connector.

Many plating alloys for connector and flexible substrate are switched to Sn-based plating alloys, because of some advantages of tin: i.e. low cost, low melting point, well solderable, high corrosion resistant and reliable electric interconnection for connector products. However, tin metallic whiskers are spontaneously formed on the tin surface. This is a major disadvantage in use of tin for electrical application. These whiskers have caused detrimental effects on electronic devices [3, 4]. In spite that the problem of the tin metallic whisker is being known over the past 50 years, the mechanism of whisker formation and growth has not been fully understood.

A number of studies reported that the whisker growth is driven by the compressive stress built up in the electroplated tin layer [5-8]. The origin of compressive stress, however, seems to be different depending upon the plating alloy, plating conditions, substrate materials and other environments (thermal cycling condition, applied external stress) [9]. Furthermore, some studies have indicated that the tin-oxide film formed on the tin surface is attributable to the whisker formation, although the direct relationship between them still remains unclear [10-12].

The whiskers grown on the Sn-Cu plating seem to be more serious than that on other lead-free plating such as Sn-Bi and Sn-Ag. In the case of Sn-Cu plating or Sn plated on a Cu substrate, numerous papers [7, 13-15] have reported that compressive stress in the tin deposit is caused by formation of Sn-Cu intermetallic compounds (IMC), such as Cu_6Sn_5. Whiskers on the Sn-Cu plating seem to grow at any conditions; even at room temperature due to the high diffusion rate of Cu and formation of IMC in Sn plating.

On the basis of very susceptible of Sn to Cu and important role of connector in electrical industries, considerable research has been carried out focusing on whiskers formed on the Sn/Cu-plated flexible substrate after contacting with the connector. In this study transmission electron microscopy (TEM) was employed to characterize microstructures in whiskers, the tin-layer and the interface between the whisker and the tin-layer in order to verify the mechanism of whisker formation and growth due to the external stress.

2. Experimental

The specimen used in this study is a Sn/Cu - plated Polyimide (PI)-flexible substrate: a tin layer about 10 μm in thickness was electrodeposited on a copper plated PI-flexible substrate. The external stress was applied on the tin surface: the Sn/Cu plated PI-flexible substrate containing 40 pins was set in a connector for 11 days at room temperature. Cross-sectional specimens of the whiskers were prepared using a focused ion beam (FIB, FB-2000K, Hitachi) equipped with microsampling unit which was operated at acceleration voltage of 30 keV with Ga^+ ion source. The tin surface was

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coated with carbon and tungsten films before the FIB fabrication to protect the specimen surface from the energetic of Ga^+ ion beam. This technique is benefit for preparing TEM specimens of the tin alloy especially of the tin whiskers. One can directly prepare a micro-sample from the area of interest; e.g. in this case, on the body or on the root of a tin whisker. The microsample was then supported with a molybdenum (Mo)-mesh. A Cu-mesh should not be used to avoid a confusion due to Sn-Cu IMC formed during FIB milling. The microsampling was done for the area far from the interface of tin/substrate (Sn/Cu) in order to hinder the incident Ga^+ ion beam on the Cu-region. Plan-view microstructure of Sn/Cu-plated PI-flexible substrate was observed with a scanning electron microscope (SEM) and a FIB-scanning ion microscope (FIB-SIM). Cross-sectional microstructure characterization of the whisker and electroplated tin-layer was performed by means of a conventional TEM (FEI TEM-F20), high resolution TEM (HRTEM), two-dimensional elemental mapping by scanning-TEM-energy-dispersive x-ray spectroscopy (STEM-EDXS).

3. Results and discussion

3.1. Plan-view microstructures

Typical SEM micrographs of Sn/Cu-plated PI-flexible substrate are shown in Fig. 1. Due to the mechanical contact between Sn/Cu-plated PI-flexible substrate and a connector, the locally stressed-area is formed as a hollow on each pin of the Sn/Cu-plated PI-flexible substrate with the average diameter of about 125 μm as indicated in the encircled areas in Fig. 1 (a). The whiskers formed on the Sn/Cu-plated PI- flexible substrate are randomly distributed with a higherSn/Cu plated PI - flexible substrate with the average diameter density at the edge of the hollow comparing with that at the area far from the hollows, as is clearly displayed in a magnified image of a hollow on a pin (Fig. 1 (b)). It is found that the whiskers formed on the Sn/Cu-plated PI-flexible substrate can be divided into three types: i.e. columnar, nodule and filament as represented in Fig. 2. The density of the filament-type whisker is relatively low comparing with the other two types. Interestingly, the whisker surfaces with and without striations were observed. The whisker surfaces without striations seemed to grow from a single grain, whereas those with striations might be resulted from nucleation on multiple grains [16]. In the following TEM results, characterization of microstructures in each type of whisker will be described and discussed in detail.

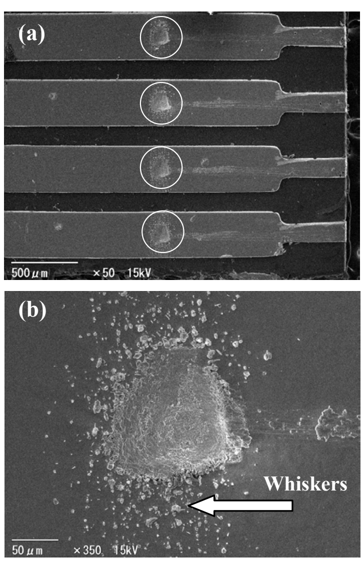

Fig. 1 SEM images of the Sn/Cu plated PI-flexible substrate surface. (a) Locally stressed-areas formed on some pins indicated in encircle areas and (b) magnified image of the

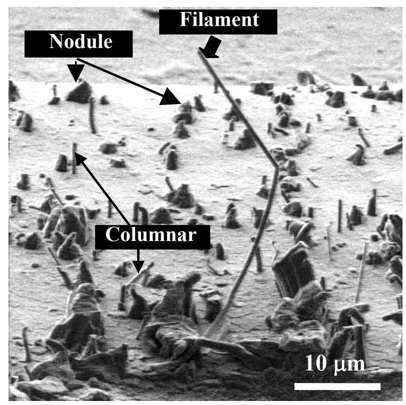

Fig. 2 FIB-SIM images showing the morphology of columnar, nodule and filament types of whisker.

3.2. Cross-sectional microstructures

3.2.1. The columnar-type whisker

In this study, the microstructure of whisker was observed from various zone-axe directions. Fig. 3 (a) shows a low - magnification cross-sectional bright-field (BF) TEM image of a columnar-type whisker with the incident beam along the $[1\bar{1}\bar{5}]$ zone axis of the whisker. Microstructure in the electroplated tin-layer is characterized by columnar grains with the average size of about 1.5 μm in width. The columnar-type whiskers with the size of about 1 μm in width and 6 μm in length are grown from the grain boundary. The whisker is kinky grown just near the surface of tin-layer with the estimated kink angle about 45° as found by LeBret *et al* [16]. On this tin surface, most of columnar-type whiskers were grown with the kink angle of 45° and 90°. A magnified image of area `A` indicated in Fig. 3 (a) is shown in Fig. 3 (b). Indexing the electron diffraction pattern (EDP) in Fig. 3 (c) that was obtained from the whisker (encircled area `c`) reveals that the whisker is a single crystal of β-Sn in the observed region at least, and the growth direction is [110]. An EDP in Fig. 3 (d) obtained from the whisker surface (encircled area

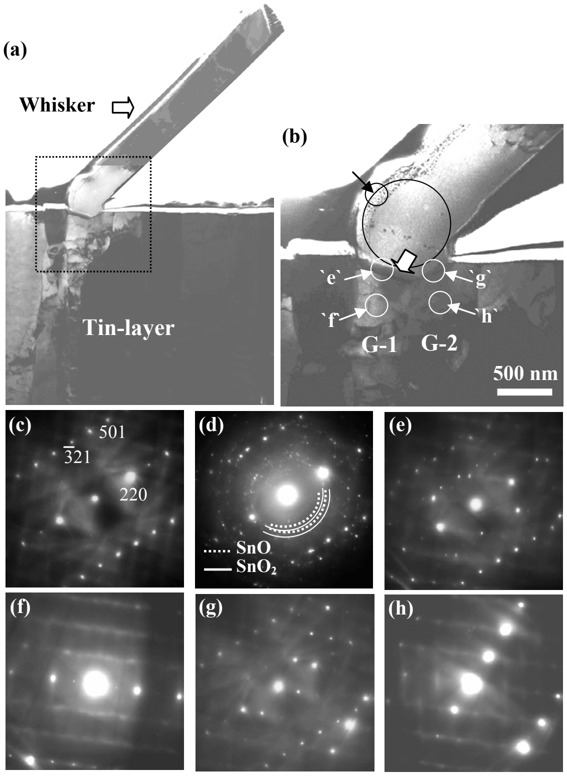

Fig. 3 (a) A cross-sectional BF-TEM image of the columnar type whisker growing on the tin-surface, (b) magnified image of area `A` indicated in Fig. 3 (a), (c-h) EDPs obtained from encircled areas `c` - `h` in Fig. 3 (b), respectively.

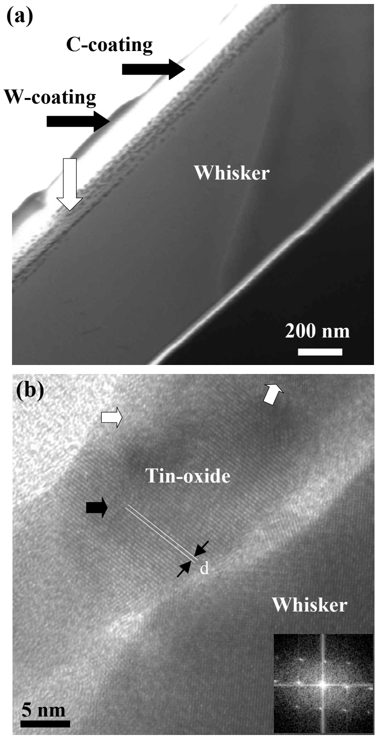

Fig. 4 (a) BF-STEM image of the whisker body showing fine dark contrast on the whisker surface and (b) HRTEM image taken from the area indicated by an arrow in Fig. 4 (a).

`d`) indicated the existence of a tin-oxide layer of polycrystalline SnO and SnO_2. The indexing of the EDP and EDXS analysis confirmed that the difference in brightness of the image contrast in grain-1 (G-1) and grain-2 (G-2) does not indicate the presence of a second phase but is due to a small tilting of the grains. The EDPs shown in Fig. 3 (e, f, g and h) indicate that the grains do not seem to have a particular relationship of crystallographic orientation. There is a hypothesis that a whisker starts to grow from a grain with a certain orientation that is not necessarily parallel to that of the whisker [17]. In addition, careful observation for the microstructure of the surface of tin-layer and whisker was carried out. The presence of SnO and SnO_2 were identified from analyses of EDPs obtained at the surface of tin-layer. The observation also suggests that the tin-oxide film formed on the surface of tin-layer is as thin as less than 10 nm [18]. Fig. 4 (a) and (b) exhibit a BF-STEM image of a part of the whisker body and a HRTEM image obtained from the area indicated by a white arrow in (a), respectively. The lattice image on the whisker surface showed the crystalline particles with various lattice spacing. Lattice spacing (d) of about 0.21 nm within the crystalline area indicated by a black arrow in (b) appears slightly wider than that in its surrounding areas such as represented by white arrows. This *d*-value is related to $(002)_{SnO}$. This is consistent with an EDP analysis in Fig. 3 (b) indicated in encircled area `d`: i.e. SnO is identified within the oxide film on the whisker surface. It is evident, therefore, that the presence of SnO particles at the vicinity close to the tin whisker surface can be attributed to the gradually oxidation of tin to be SnO then SnO_2, as suggested in our previous study [18].

3.2.2 The nodule-type whisker

Fig. 5 (a), (b) and (c) show a cross-sectional BF-TEM image of the nodule-type whisker with the incident beam along $[\bar{1}11]$ and EDPs, respectively. The micrograph indicatesthat the whisker consists of two sub-grains in the area of the micrograph. This suggests that whisker might grow with small kink. An EDP in Fig. 5 (c) obtained from the interface area between the whisker and the tin-grain as indicated in encircled area `c` does not identify crystallographic orientation relationship between them. Analyses of EDPs obtained from the interface of the whisker and the tin-grains recognized the formation of an intermetallic compound (IMC) of Cu_6Sn_5. A two -dimensional elemental

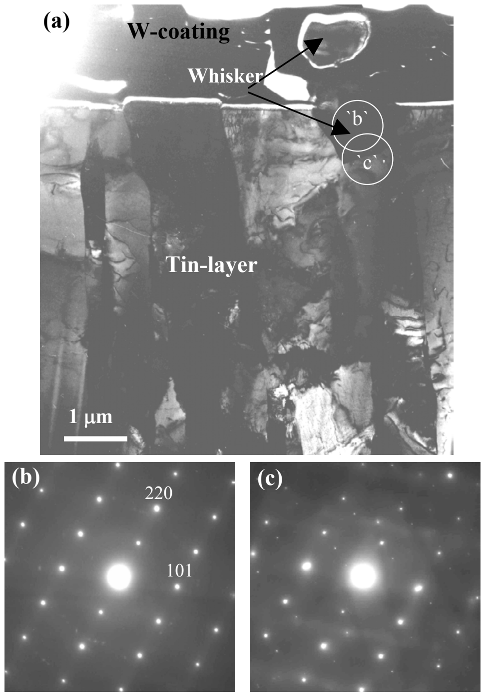

Fig. 5 (a) a cross-sectional BF-TEM image of nodule-type whisker grown on the surface of tin-layer, (b) and (c) EDPs obtained from the whisker and the interface of the whisker and a columnar tin-grain as indicated in the encircled regions `b` and `c`, respectively.

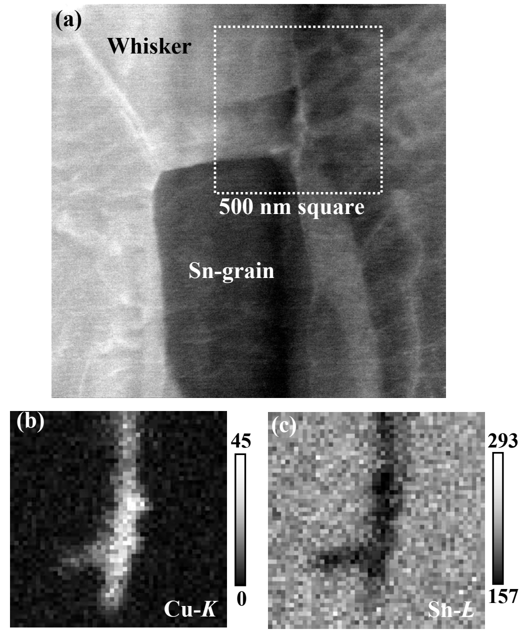

Fig. 6 STEM-EDXS elemental mapping. (a) BF-STEM image showing a nodule-type whisker grown on the Sn-grain, (b) Cu-map and (c) Sn-map.

mapping by STEM - EDS in Fig. 6 demonstrates that in the square area at the interface of the whisker and the tin-grains, Cu rich area in Fig. 6 (b) is overlapping with Sn rich area in Fig. 6 (c). This confirms the presence of Cu-Sn phase IMC.

3.3.3 The filament-type whisker

As mentioned above, the number of filament-type whiskers was relatively small compared with those of other two. The filament-type whisker was grown longer than 30 μm with an irregular shape. It is very difficult to prepare a TEM specimen by a FIB microsampling technique. To study microstructure of this whisker, a microsample was only taken from the whisker body. EDPs obtained from the body of the filament-type whisker indicated that this whisker is of a single crystalline β-Sn growing at the [101] direction.

3.3.4. Relationship between the external stress and whisker-growth

According to SEM and TEM observation results of the whiskers grown on the Sn/Cu-plated PI-flexible substrate, the mechanism of whisker formation and growth can be considered as follows. The whiskers grown on the Sn/Cu-plated PI–flexible substrate were observed after inserting the flexible substrate into the connector for 11 days at room temperature. Therefore, it should be noted that the whisker-growth is not caused by the thermal stress or electrical current, but by the external stress generated from the mechanical contact between the connector and tin surface of the Sn/Cu-plated PI-flexible substrate. Due to applied external stress on the tin-surface, locally stressed-areas are formed as a hollow on each pin as has been demonstrated in Fig. 1 (a). Edge part of hollows is thought to have higher stress than the area far from the edge of hollow.

In the present condition, whiskers were grown from the surface of Sn/Cu with the preference directions of [110] and [101] as reported in other study [19]. It has been reported that the whisker-growth could occur only if the formation of IMC induces the compressive stress in electroplated tin-layer [20]. Although at room temperature Cu atoms will diffuse into the tin-layer and then form a Sn-Cu IMC phase at the interface of Sn/Cu, the compressive stress would not be built up in the tin layer without the presence of the applied external stress or the thermal treatment. Consequently, no whisker would be found on the tin surface.

In this study, the formation of Sn-Cu IMC has been identified at the boundaries between the nodular-type whisker and the tin-grains, but not at the boundaries areas of columnar-type whisker in the observed area. It can be understood, therefore, that highest stress at the edge of hollow contributes to the formation of nodular-type whiskers. During mechanical contact between tin-surface of the Sn/Cu-plated PI-flexible substrate and the connector, Cu atoms across the Sn-Cu IMC layer then diffuse into the tin layer toward the grain boundaries and form Cu_6Sn_5 IMC. Then the compressive stress originated from Cu_6Sn_5 IMC will build up within the tin-layer and drive the diffusion of Sn atoms from the tin-grain into the grain surface to form the whisker.

Related to the columnar-type whiskers growing from the grain boundary, their formation can be considered to start with the recrystallization. In some cases, external stress assists the recrystallization. Especially for the anisotropic characterization of tin metal, stress will be possible to concentrate on some grains. The concentrated stress will assist the recrystallization. If the orientation of such grains is favorable for the formation of whisker, the recrystallized grain will grow as a whisker. In this study, it is supposed that the filament-type whisker was formed with the similar mechanism to the columnar-type whisker. But, the difference in length between the whiskers cannot be clarified from these experimental results.

The oxide-layer on the tin surface is considered to play a role of a capped layer against the internal stress and to produce stress in the tin grains associated with proceeding of oxidation. The strength of layer and the amount of stress is strongly related to the microstructure of layers which are made of SnO and SnO_2. Further study would be necessary.

4. Conclusions

The microstructures of whiskers that are spontaneously grown on the tin surface after inserting the Sn/Cu-plated PI-flexible substrate into the connector have been characterized as follows.

1. Three kinds of whiskers are observed; nodule, columnar and filament-types whiskers. These whiskers are randomly distributed in the locally stressed area around a hollow on each pin. The density of the whiskers is higher at the edge of hollow compared with that in the area far from the hollow. It is considerable attributed to the higher stress at the edge of hollow. This indicates that the applied stress directly contributes to the formation of whiskers.
2. The whiskers are almost single crystalline β–Sn phase and grown with the preferred direction of [110] and [101].
3. Precipitates of Cu_6Sn_5 are formed at the boundaries of tin-grains on which the nodule-type whisker are grown. This strongly suggests that the nodule-type whiskers are grown with an assist of stress due to the formation of IMC phase.
4. The columnar and filament-type whiskers stand on a boundary of tin-grains. This suggests that diffusion of Sn atoms along the boundary would be related with the formation of these whiskers. In addition, an oxide layer is apt to be broken at the boundary, so that tin atoms would be able to exclude to be a whisker.
5. The presence of SnO within the tin-oxide film would be an important point in affecting whisker formation.

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