Mechanism of Generation and Suppression of Tin Whiskers on Tin and Tin-Lead Plated Films

Koji Murakami, Masako Okano, Makoto Hino, Masao Takamizawa and Kiyomichi Nakai

1Industrial Technology Research Institute of Okayama Prefectural Government, Okayama 701-1296, Japan
2OM Sango Co., Ltd., Okayama 700-0971, Japan
3Graduate School of Science and Engineering, Ehime University, Matsuyama 790-8577, Japan

Generation and growth of whiskers and nodules from electroplated tin and tin-lead films on copper or nickel substrates were studied by scanning electron microscopy and X-ray diffraction. In the case of copper substrates, whiskers were formed in 0.3 Ms on the tin film whose thickness was 1 μm. On the other hand, tin-lead films on copper substrates showed only nodules even after 13 Ms. Residual stress of the tin film (1 μm) and the number of whiskers increased with the amount of copper-tin intermetallic compounds (Cu₆Sn₅) which developed between the plated film and the copper substrate. Although residual stress and the amount of Cu₆Sn₅ also increased in the tin-lead system, the morphology of the layer of Cu₆Sn₅ was more uniform compared with the case of tin films on copper substrates. When the tin-lead film was subjected to the compression testing by a ball of zirconium oxide (1 mm-diameter, 2.94 N–0.605 Ms), the edge of the indentation did not show any whiskers but diffusion of lead was observed from right under the zirconium oxide ball to the fringe, as well as Ostwald growth of lead. In the case of the tin film on the nickel substrate, whose residual stress was weakly tensile, nickel-tin intermetallic compounds (Ni₃Sn, Ni₅Sn₃, Ni₅Sn₄) uniformly developed immediately after electroplating, and no whiskers were observed even after the compression testing. While growth of whiskers is considered to be due to diffusion of tin atoms induced by inhomogeneous strain field in the electroplated film, lead atoms in tin-lead system is considered to diffuse rapidly toward the free surface to release residual stress and to generate many nodules.

Keywords: tin electroplating, tin-lead electroplating, whisker, nodule, intermetallic compound, local strain, diffusion, oxide film

1. Introduction

Electroplated films of tin and tin-based alloys are widely used in electronic circuits for their good conductivity on connectors and lower cost compared with that required for plating of gold. However, short circuits in narrow pitch connectors have been critical because of whiskers which develop on plated surfaces in needle-like shape. Although electroplating of tin-lead alloy was reported to successfully suppress whiskers in the 1950’s and have been utilized until recently, use of lead must be replaced by other measures from the standpoint of RoHS (Restriction of Hazardous Substances) directives. Therefore, suppression of whiskers by appropriate alloying elements and microstructural control is currently an urgent matter in electronic devices.

In the previous report on electroplated tin films on copper substrates, effect of nonuniformity of residual stress caused by development of copper-tin intermetallic compounds and that of oxide films on generation of whiskers were discussed. The proposed mechanism is summarized as below.

1. As Cu₆Sn₅ develops nonuniformly, nonuniform distribution of strain or gradient of free energy is formed in tin films.
2. Diffusion of tin atoms into low-energy grains causes decrease of atomic vacancy there.
3. Bulging of the grains toward the surface is required when concentration of atomic vacancy recovers to the thermally equilibrated value. This occurs on the areas where oxide films on the plated surface is fragile or surface tension is low.
4. Nodules are thus formed, then, these develop into whiskers when tin atoms continue to flow into the root grains and creation-annihilation of atomic vacancies is repeated.

In this paper, nonuniformity in plated films and substrates is further researched, and mechanism of suppression of whiskers by lead is discussed from the viewpoints of nonuniformity in the system and mass transfer.

2. Experimental

Electroplatings of tin and tin-lead were conducted in alkanol sulfonic acid-based baths according to the previous report. Concentration of lead is 10 mass% unless otherwise specified. Rolled sheets of copper (for Haring cell testing, Yamamoto-MS Co., Tokyo) and nickel (NI-313382, 200μm, Nilaco Corp.) were used as substrates. Nickel substrates underwent electrodegreasing and subsequent activation with nitro-hydrochloric acid (HNO₃ : HCl = 1 : 3) prior to electroplating. In the following sentences, an electroplated film of tin on the copper substrate whose thickness is 1 μm is expressed as ‘tin on copper (1 μm)’.

Surfaces of plated films were observed by field emission electron probe microanalyzer (FE-EPMA). Focused ion beam of gallium (FIB) and field emission scanning electron microscope (FE-SEM) were used for cross-sectional observation. Wettability between plated films and a molten tin-silver-copper solder (Sn-3.0 mass%Ag-0.5Cu) at 518 K was evaluated by measuring ‘zero-cross time’ in meniscographic method at which resultant of buoyant force and wetting force became zero. Concentrations of lead in the tin-lead films for the wettability testing were 0, 1, 3, 5 and 7 mass%, and six specimens were prepared for each concentration. The flux for

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the testing was a mixture of ethanol and NA-200 (Tamura Kaken Corp., 1:1 in volume).

Residual stress of plated films was measured according to previous report 3,4) by microfocus X-ray diffractometry (wavelength $\lambda_{CuKα} = 0.1542$ nm, beam diameter 300 $\mu$m, oscillation $\Delta x, \Delta y = 0.5$ mm) with two-dimensional detector 6-9). For evaluation of formation of nodules and whiskers induced by external force, compression testing 3) was conducted where a zirconium oxide ball of 1 mm in diameter was indented onto plated films (load 2.94 N, testing time 0.605 Ms). In the following sentences, the zirconium oxide ball is expressed as ‘indenter’. A microtome was used in specimen preparation for cross-sectional observation, where a glass knife was used in coarse cutting, then, a diamond knife (edge angle 45°, final feed 50 nm, cutting velocity 0.1 mm/s) in final cutting.

For three-dimensional evaluation of the microstructure of Cu$_6$Sn$_5$ near a whisker, serial sectioning was conducted by repeating Fig. 1(c),(d). Two rectangular marks were placed by FIB at the corners of the observation area for adjusting the position and rotation angle. A feed in microtome per observation was 100 nm, and 50 scanning ion micrographs (SIMs) were taken. Here, additional FIB fabrications were conducted as the sectioning proceeded and the original markings became shallow. A software IMOD 10) was used for reconstruction of three-dimensional images of the substrate, Cu$_6$Sn$_5$, the whisker and its root grain from the above SIMs obtained by serial sectioning. In this process, the copper substrate, Cu$_6$Sn$_5$, the whisker and the root grain in each SIM were painted in corresponding colors by photo retouching software for improving the accuracy in area recognition of IMOD. After three-dimensional reconstruction for the above parts, these objects were joined to be shown in one image.

3. Experimental Results

3.1 Temporal change of plated film and effect of lead

Figure 2 shows the X-ray diffraction patterns of tin on copper and tin on nickel (1 mm). As previously reported 3), Cu$_6$Sn$_5$ is formed after keeping for 0.950 Ms under ambient conditions in the case of tin on copper (Fig. 2(b)). In the case of tin on nickel, nickel-tin intermetallic compounds of Ni$_3$Sn, Ni$_3$Sn$_2$ and Ni$_3$Sn$_4$ were identified even in the as-plated specimen (Fig. 2(c)).

Figure 3 shows secondary electron images (SEIs) and backscattered electron image (BEI) of the surfaces of tin on copper, tin on nickel and tin-lead on copper (1 mm). Whiskers and nodules were observed on the surface of tin on copper after keeping for 0.605 Ms under ambient conditions (Fig. 3(a)). In the case of tin on nickel, prominent grains of a few $\mu$m in size were observed on the as-plated surface, but neither whiskers nor nodules were formed (Fig. 3(b)). Many nodules were observed in the SEI on the surface of tin-lead on copper (Fig. 3(c)). Here, nodules of lead are...
recognized as brighter grains in Fig. 3(d), encircled by broken line, and those of tin by solid line.

Figure 4 shows the cross-sectional microstructures (SIM and BEI) of tin on copper, tin-lead on copper and tin on nickel (1 μm). In the case of tin on copper (Fig. 4(a)), Cu₆Sn₅ developed nonuniformly along the grain boundaries of tin, and changes of brightness in the SIM due to local deformation are observed. On the other hand, Cu₆Sn₅ developed uniformly and coarse grain of Cu₆Sn₅ was not observed in the case of tin-lead on copper (Fig. 4(b)).
compared with that of tin on copper (Fig. 4(a)). However, changes of brightness in copper near Cu$_6$Sn$_5$ due to local deformation were observed as the case of tin on copper (Fig. 4(a)). In the case of tin on nickel (Fig. 4(c)), formation of a nickel-tin intermetallic compound is observed between the plated film and the substrate, and the layer was more uniform than that of Cu$_6$Sn$_5$ in tin on copper. Here, BEI was used for tin on nickel since the difference of brightness in SIM between the intermetallic compound and the plated film was not large enough to distinguish the two phases.

Figure 5 shows the temporal changes in residual stresses of tin in tin on copper, tin-lead on copper and tin on nickel (1 µm). In the case of tin on copper, residual compressive stress rapidly changed until ~1 Ms after plating, then, asymptotically reached 40–50 MPa. On the other hand, in the case of tin-lead on copper, absolute values and temporal change of residual stress were smaller than those of tin on copper. In the case of tin on nickel, residual stress of tin was ~5 MPa (tensional), and its temporal change was quite small.

Figure 6 shows the reconstructed three-dimensional microstructures near a whisker in tin on copper (1 µm) obtained by serial sectioning. Since the whisker was separated from the root grain as sectioning proceeded, the entire shape of the whisker is not visualized. Therefore, a part of the whisker and the root grain are shown as a set of wireframe in Fig. 6(b). Figure 6(a) shows the Cu$_6$Sn$_5$ develops mainly along the grain boundaries of tin is not in a complete network structure, but develops nonuniformly in granular shape. Figure 6(b) shows that Cu$_6$Sn$_5$ exists near the root grain rather than just beneath the whisker. In the cross-sectional SIMs, one of which is Fig. 4(a), most of tin grains were equiaxial whose size was ~1 µm, but the root grain extended to ±z-direction in Fig. 6(b).

Figure 7 shows the zero-cross times of tin and tin-lead films immersed into the molten solder. The zero-cross times of the tin-lead films which contained 1 mass% lead were less than half of those of tin, that is, wettability was largely improved by addition of lead. However, wettability did not show meaningful changes among the specimens which contained lead. Figure 7 also shows that zero-cross time of tin varied largely compared with the case of tin-lead.

3.2 Change of plated film by external force

Figure 8 shows the surface and cross-sectional microstructures of tin-lead on copper (5 µm) and tin on nickel (1 µm) after compression testing. In the case of tin-lead on
copper (Fig. 8(a)), lead grains, which correspond to brighter areas in BEI, were not observed at the center of the indentation. On the other hand, lead grains at the fringe within the indentation (Pb(2) in Fig. 8(a)) were coarser than those observed in the areas distant from the indentation (Pb(1)). In Fig. 8(b), the cross section of Fig. 8(a), coarse grains of lead (Pb(5)) were observed in the plated film at the fringe of the indentation. Coarse grains of lead were also found in the plated film distant from the indentation (Pb(3)), and the interface between the plated film and the substrate was partly occupied by lead (Pb(4)). In the case of tin on nickel (Fig. 8(c)), many nodules were formed near the indentation, but no whisker was observed.

Figure 9 shows the electron backscattering diffraction (EBSD) patterns of tin obtained on the cross section of tin on copper after cutting by glass knife (Fig. 9(a),(b)) and diamond knife (Fig. 9(c)). Fast Fourier transformation (FFT) images of the poles indicated by broken lines are shown in the upper-right corners of the EBSD patterns. FFT images, which show the sharpness of EBSD patterns, semi-quantitatively show crystallinity of the material at which electron beam is irradiated. That is, extension of an FFT image toward the high-frequency region corresponds to higher crystallinity.11) Here, FFT images were obtained at the poles for enhancement of their isotropy. The EBSD pattern of copper on the section obtained by glass knife (Fig. 9(a)) was diffuse, and the high-frequency component in the corresponding FFT image was weak. On the other hand, the EBSD pattern of tin on the section obtained by diamond knife (Fig. 9(b)) was as sharp as that obtained by diamond knife, showing a similar extension toward high-frequency region in the FFT images.

4. Discussions

4.1 Suppression of whisker by lead

Part of lead in tin-lead films is dissolved in the matrix of tin, and other part of lead exists as precipitates which contain tin, observed as brighter areas in BEIs of Fig. 3, 8. In the following sentences, the former is expressed as ‘dissolved lead’, and the latter ‘precipitated lead’. From Fig. 3, whiskers are not observed in the case of tin-lead on copper, but many nodules are formed. Since nodules of tin are formed on the areas where oxide films do not exist or it is fragile,3) the entire surface of the tin-lead film is thought to be covered with fragile oxide films. This corresponds to the improvement of wettability by lead (Fig. 7), that is, oxide films are lost immediately, then, the reaction between the plated film and the molten solder begins in a brief period. From the point that wettability was not further improved with respect to the amount of lead, the fragility of oxide films is thought to be caused by dissolved lead or enrichment of lead at the surface.

Regarding the morphology of Cu₆Sn₅, uniform layers tend to be formed when lead exists in the system (Fig. 4(b)). In the case of the tin-lead film kept for 8.64 Ms after plating, the layer of Cu₆Sn₅ developed more uniformly than that obtained in the case of the tin film.5) The uniform layer is thought to reduce the nonuniformity of strain or gradient of free energy which causes migration of tin atoms. When Cu₆Sn₅ nucleates and grows uniformly to form a uniform layer, copper atoms must pass through the layer of Cu₆Sn₅ before they reach the tin film. Although diffusion coefficient of copper in Cu₆Sn₅ has not been determined yet, thickness of the layer of Cu₆Sn₅, formed in tin on phosphorus bronze (6 µm) kept either for 0.864 Ms or 8.64 Ms, was ~1 µm.5) This tendency has also
been confirmed in the specimen used in another previous report, where thickness of Cu₆Sn₅ formed in tin on copper (10 μm) was ~1 μm after 30 Ms. From these points, diffusion coefficient of copper in Cu₆Sn₅ is thought to be quite small at room temperature, compared with that of copper in tin. When Cu₆Sn₅ develops nonuniformly, copper atoms are supplied into tin through the interface where Cu₆Sn₅ is not formed, that is, where the tin film directly contacts the copper substrate. On the other hand, when a thin and uniform layer of Cu₆Sn₅ is formed to separate the tin film from the substrate, growth of Cu₆Sn₅ is thought to stop virtually because of the quite low diffusion rate of copper in it.

Here, effect of lead on formation of Cu₆Sn₅ is discussed. When copper atoms migrate into tin, and tin is oversaturated with copper, Cu₆Sn₅ is formed to decrease chemical free energy in the area. The preferred nucleation site of Cu₆Sn₅ is thought to be the interface between tin and copper or grain boundary of tin. If lead promotes uniform nucleation of Cu₆Sn₅ on the interface between tin and copper, formation mode of Cu₆Sn₅ in Fig. 4(b) can be explained. In Fig. 8(b), precipitated lead tends to exist near the interface between the plated film and the substrate (Pb(4)), but precipitated lead as a nucleus of the formation of Cu₆Sn₅ was not obviously observed. From the phase diagram of tin-lead binary system, the maximum amount of dissolved lead in tin is less than 1 at% at room temperature. The above observation of lead suggests that the dissolved lead strongly contributes to the uniform nucleation of Cu₆Sn₅.

Impurity elements which exist in the matrix as solute are known to have effects on the morphology of interface in reactive diffusion. One of the examples is the growth of α-Fe into the layer of Fe₂Al₅ formed on an iron substrate with a strong fiber texture (c-axis // substrate normal). When high-purity iron is used as substrates, α-Fe nonuniformly nucleates and grows in a columnar shape, but uniform nucleation of α-Fe occurs and the α-Fe layer uniformly develops in the case of ferritic stainless steel. From this point of view, dissolved lead in tin-lead system reasonably affects the nucleation of Cu₆Sn₅.

Formation of Cu₆Sn₅ is accompanied by local volume change and strain, which can be observed as the change of brightness in SIMs (Fig. 4(a),(b)) especially at the copper substrate. This local strain is thought to exist also in tin films, therefore, nonuniform formation of Cu₆Sn₅ induces gradient of free energy as previously discussed. Even when lead exists in the system, formation of Cu₆Sn₅ causes strain in plated films and substrates. However, the gradient of free energy is moderate compared with the case of tin on copper, since Cu₆Sn₅ uniformly develops because of lead. That is, lead is thought to have a function to promote uniform formation of Cu₆Sn₅ and to moderate the gradient of free energy which causes migration and accumulation of tin.

Fig. 9 Electron backscatter diffraction patterns and fast Fourier transformation of broken squared region. (a) Cu cut by glass knife, (b) Sn cut by glass knife, (c) Sn cut by diamond knife.
Next, behavior of precipitated lead is discussed. When tin-lead on copper is kept under ambient conditions, many nodules are formed as observed in Fig. 3(c),(d). This is thought to be caused by local strain due to formation of Cu₆Sn₅ at the interface between the plated film and the substrate, and resulting migration of lead toward the surface for stabilization. Part of lead exists at the interface supposedly because interfacial energy decreases when the interface is occupied by lead. It is also thought that in the areas where lead lies between the plated film and the substrate, strain caused by formation of Cu₆Sn₅ is smaller than that of other areas. Thus, the system is stabilized by considering interfacial and strain energy.

From Fig. 8(a),(b), lead migrates from highly stressed areas to relaxed ones when the system is under external force. Figure 5 shows a moderate temporal change of residual stress in the case of tin-lead on copper, compared with the case of tin on copper. These suggest that lead easily migrates in tin films and the speed is higher than that of tin. Here, the diffusion rate of lead at the phase boundary in tin-lead binary system is known to be larger than that of tin. From these points, major migrating element in the system of tin-lead on copper is thought to be lead, and migration of tin which causes formation and growth of whiskers can be suppressed by rapid migration of lead from highly strained area to stable ones which relaxes nonuniformly compressed state of tin. Although migration of tin and formation of nodules are inevitable as shown in Fig. 3(c),(d), this mode of change in plated surfaces does not cause short circuits practically, if many nodules are formed due to fragile oxide films. Figure 10 shows schematic illustration of the temporal change in the system of tin-lead on copper discussed above.

4.2 Local deformation caused by intermetallic compound and effect of external force

From Fig. 4, Cu₆Sn₅ is formed in the plated film, causing strain due to the difference of density between tin and Cu₆Sn₅. When tin whose volume is V_{Sn} is transformed into Cu₆Sn₅ whose volume is V_{Cu₆Sn₅}, by the supply of copper from the substrate, the ratio is given by eq. (1).

\[
\frac{V_{Cu₆Sn₅}}{V_{Sn}} = \frac{1}{5} \frac{\rho_{Sn} M_{Cu₆Sn₅}}{\rho_{Cu₆Sn₅} M_{Sn}} = 1.44
\]  

Here, density and atomic mass of each substance are \(\rho_{Sn} = 7.287 \times 10^{3} \text{kg/m}^3\), \(M_{Sn} = 118.69 \times 10^{-3} \text{kg/mol}\), \(\rho_{Cu₆Sn₅} = 8.430 \times 10^{3} \text{kg/m}^3\), \(M_{Cu₆Sn₅} = 991.25 \times 10^{-3} \text{kg/mol}\). From eq. (1), transformation of tin into Cu₆Sn₅ is accompanied by the increase in volume and induces local compressive strain in tin near Cu₆Sn₅. Strain caused by the above deformation is thought to exist in the areas of the substrate which contact the plated film. Thus, the brightness change at the substrate in Fig. 4 is brought about by this local deformation near Cu₆Sn₅.

In the previous report, recovery, recrystallization and grain growth were shown to occur in tin films at room temperature. From Fig. 9, dislocations generated by the sectioning with glass knife are thought to disappear through recovery and recrystallization, since clear EBSD patterns of tin can be taken on the section. Density of dislocation is reduced by cancellation of dislocations of opposite signs, climbing up of edge dislocations, and glide toward the surface. When the dislocations generated by sectioning and formation of Cu₆Sn₅ disappear on the surface for cross-sectional observation, strain or brightness change in SIM may not be clearly visible for tin, compared with that observed in the copper substrate. However, state of strain in tin can be estimated qualitatively if strain of copper is tensional just beneath Cu₆Sn₅ and compressive near the area.

From Fig. 2, while Cu₆Sn₅ is formed in the system of tin on copper under ambient conditions, Ni₅Sn₃, Ni₃Sn₅ and Ni₃Sn is formed in the case of tin on nickel. Figure 4 shows that a uniform layer of an intermetallic compound is formed in the latter case, and residual stress of tin caused by the intermetallic compound layer is weakly tensional (Fig. 5). Crystallographic coherency between the intermetallic compound and tin as well as change in volume can cause local strain. Although the major factor for local strain is not determined here in the case of tin on copper, coherent strain is thought to exist in the system, since residual stress is detected even when tin and lead atoms migrate and nodules and whiskers are formed adequately. In the system of tin on nickel, strain caused by volume change or coherency is thought to be small, and only nodules are formed when the system is compressed by external force (Fig. 8(c)). From these points, the external force in this compression testing is not the main factor for generation of whiskers, but only assists their formation and growth.

4.3 Change in free energy by formation of nodule

In the previous report, change in free energy was discussed in the process where a whisker grows forming new surface and volume. Here, the modal shift of growth, whether bulge of a nodule or extension of a whisker at the root, is treated for tin films by evaluation of the change in surface energy.

Figures 11(a)–(d) schematically shows the cases where a nodule is formed by bulging of the flat surface (contact angle \(\theta\)) and a whisker is extended by \(\Delta S\) at the root. Surface area of the nodule \(S^{(n)}\) and the volume \(V^{(n)}\) are given by eqs. (2) and (3), respectively, using radius of the root grain \(r\) and contact angle \(\theta\).

\[
S^{(n)} = \frac{\pi r^2}{\cos^2 \theta} \quad V^{(n)} = \frac{\pi r^3}{3} \cos^2 \theta
\]
As discussed in the previous report, tin is thought to migrate toward low-energy region through grain boundaries, surfaces and dislocations, as well as atomic vacancies. When the migrating tin atoms flow into a grain, vacancies in the grain are occupied by the tin atoms, then, concentration of vacancy continues to decrease. However, this state is unstable since vacancy concentration is lower than thermally equilibrated value, therefore, vacancy concentration must recover. Increase of vacancy is thought to cause bulging toward the surface, and grains with small strain become nodules or root grains of whiskers.

Regarding this process, changes in surface morphology and energy are formulated as follows. In the initial state, the vacancy concentration has been reduced to certain value, then, the number of vacancy in the grain increases by $\Delta n$. The number of tin atoms in the root grain $N$ and increase in vacancy $\Delta n$ are related by $\alpha$ in eq. (4).

$$\Delta n = \alpha N$$

If the volume of vacancy $v_v$ is equal to that of tin atom, the volume of the nodule and the increase of vacancy satisfy eq. (5), and the relation between $\alpha$ and $\theta$ is given by eq. (6).

$$V^{(n)} = v_v \Delta n$$

$$\alpha = \frac{\pi r^3}{3v_vN} \frac{(1 - \cos \theta)(2 + \cos \theta)}{\sin \theta(1 + \cos \theta)}$$

Although solving eq. (6) analytically to express $\theta$ as a function of $\alpha$ is difficult, eq. (6) can be approximated as eq. (7), since the profile shows good linearity at $0 \leq \theta \leq \pi/4$.

$$\theta \approx \frac{8 \alpha}{\pi}$$

Here, the parameters in the coefficient of eq. (6) was set as $r = 0.5 \mu m$, $v_v = 2.7 \times 10^{-29} m^3$, $N = 2.9 \times 10^{10}$.

The increase in surface energy caused by formation of a nodule is expressed as eq. (8) using the specific energy on the surface of plated films $\gamma$.

$$\Delta G_s^{(n)} = \gamma \left( \frac{2\pi r^2}{1 + \cos \theta} - \pi r^2 \right)$$

$$= \pi r^2 \gamma \left[ \frac{1 - \cos \theta}{1 + \cos \theta} \right]$$

Surface tension $\gamma$ can be interpreted as stability or fragility of surface, but the value can not be accurately evaluated. Therefore, normalized form of eq. (8) by $\gamma$, $\Delta g_s^{(n)}$ (eq. (9)), is used in the following discussion.

$$\Delta g_s^{(n)} = \frac{\Delta G_s^{(n)}}{\gamma} \approx 7.9 \times 10^{-13} \frac{1 - \cos(8\alpha)}{1 + \cos(8\alpha)}$$

Here, $\theta$ in eq. (8) is replaced by $\alpha$ in eq. (7). Regarding the extension of a whisker in Fig. 11(c), (d), the change in surface energy is given by eq. (10), according to the previous report.

$$\Delta g_s^{(w)} = \frac{\Delta G_s^{(w)}}{\gamma} \approx 3.1 \times 10^{-12} \alpha$$

From Fig. 11(e), $\Delta g_s^{(w)}$ is proportional to $\alpha$ in the extension of the whisker at the root, but the initial increase of $\Delta g_s^{(n)}$ is smaller, that is, $\Delta g_s^{(n)} \ll \Delta g_s^{(w)}$ for $\alpha \sim 0$. This means that formation of nodule is more advantageous than extension of whisker when the same amount of vacancy is increased. Although small $\gamma$ brings about frequent formation of nodules, $\Delta g_s^{(n)}$ exceeds $\Delta g_s^{(w)}$ as $\alpha$ increases. Therefore, nodules bulge or $\theta$ increases at the initial stage, then, the growth mode shifts to extension at the root. The modal shift occurs at $\alpha = 0.175$ or $\theta = 1.4$ rad when $\Delta g_s^{(n)}$ intersects $\Delta g_s^{(w)}$. Although eq. (7) becomes an incorrect approximation for this region of $\alpha$, the above discussion can well explain the actual phenomenon, since the tips of many nodules and whiskers are observed to be hemispherical by microscopy.

5. Summary

In this paper, nonuniformity of microstructure in the systems of tin plated films on copper substrates, tin-lead on copper and tin on nickel was investigated. Mechanism of suppression of whiskers by lead was explained from the viewpoints of intermetallic compounds, oxide films and mass transfer of lead. The shift in growth mode of whisker was discussed by formulating the change of surface energy for nodule and whisker. The results are summarized as follows.
Lead in tin-lead on copper is dissolved in tin matrix and precipitated on grain boundaries of tin. Dissolved lead is thought to promote uniform nucleation and growth of Cu$_6$Sn$_5$, and formation of fragile oxide films.

Since formation of Cu$_6$Sn$_5$ in plated films is accompanied by increase of volume, compressive strain is induced in the surrounding tin. Although the strain in tin may disappear on the section, copper shows brightness change in SIM which indicates local strain and suggests similarly strained state of tin.

Precipitated lead migrates to relax strain according to the nonuniform strain or the gradient of free energy caused by formation of Cu$_6$Sn$_5$ or external force. In the case of tin-lead on copper, nodules of lead as well as tin are formed, and remarkable migration and Ostwald ripening of lead are observed after compression testing.

Formulation of change in surface energy caused by formation of nodule and extension of whisker showed that nodules can easily be formed when oxide films are fragile or the surface tension is low. It also explained that the root of whisker begins to extend after nodule bulges to certain contact angle.

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REFERENCES