Mechanism of Generation and Growth of Whiskers on Tin Electroplating*

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Generation and growth of whiskers on tin electroplating was studied by scanning electron microscopy and X-ray diffraction. When the surface of the plating, whose thickness was 1 μm , was etched by argon ion beam to remove native oxide scale and kept in a vacuum, whiskers were rarely observed but many nodules were formed. While residual stress of tin plating (1 μm) and the number of whiskers increased with the amount of Cu_6Sn_5 formed between the tin plating and copper substrate, the 10 μm thickness specimen showed no meaningful change and no whiskers were found. The orientation of whiskers was shown to be identical throughout a crystal by electron backscattering diffraction even when kinked. The mechanism of generation and growth of whiskers is considered to be due to diffusion of tin atoms induced by inhomogeneous strain field, formation of vacancies, and the resulting increase in volume of the grain receiving the tin atoms. Energy change in the growth of whiskers was modelled and calculated, and the main factor determining the growth was found to be the formation enthalpy of a vacancy and the entropy of configuration. [doi:10.2320/matertrans.MRA2008236]

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1. Introduction

Electroplating of tin, its alloys and gold has been widely used for the purpose of good conductivity of terminals in electronic circuits as well as good wettability with solder. Pure tin is the most preferable from the viewpoints of low environmental load, low cost and less consumption of natural resources, but short circuits can be caused by whiskers which can grow from electroplated tin films to be needles of $\sim 1 \mu\text{m}$ in diameter and $\sim 10^2 \mu\text{m}$ in length. Since the interval of the terminals has become narrower ($\sim 10^2 \mu\text{m}$) in smaller and lighter portable electronic equipment, suppression of whiskers is urgently required for assuring long-term operation of electronic devices.

Figure 1 shows a schematic illustration of whiskers morphology frequently observed on films of electroplated tin and its alloys. While whiskers grow in morphologies such as straight (Fig. 1(a)), kinked (Fig. 1(b)) and curved (Fig. 1(c)), nodules (Fig. 1(d)) are frequently observed, which seem to have ceased growing at an early stage of generation and growth of whiskers. Practically, whiskers of Fig. 1(a), 1(b), 1(c) mainly cause short circuits. The above problem which was first found in telephone exchanges in the 1940's¹⁾ was prevented by electroplating of tin-lead alloy without clear theory for explaining formation and growth of whiskers from the standpoint of materials science. In tin-lead system, only nodules (Fig. 1(d)) form which do not cause short circuits,²⁾ but recently RoHS directives (Restriction of Hazardous Substances) strictly ban the use of lead. Therefore finding other elements which can successfully substitute lead through detailed research on formation and growth of whiskers, as well as optimal control of microstructure of tin alloys, are necessary.

As factors which cause or affect whisker, residual stress of electroplated films, dislocations, native oxide scale, inter-

Fig. 1 Schematic illustration of morphology of whisker. (a) Straight, (b) Kinked, (c) Curved, (d) Nodule

metallic compounds which develop at the interface between electroplated film and substrate, preferred orientation in growth of whiskers are proposed. Since these factors also interact in a complex manner, it is extremely difficult to discuss every factor independently to uniquely determine the cause of formation and growth of whiskers. In this paper, the effect of native oxide scale on morphology and number of whiskers, the relationship between intermetallic compound and residual stress, and change in crystal orientation at the root of whiskers were researched. The mechanism of formation and growth of whiskers is discussed from the viewpoint of mass transfer of tin.

2. Experimental

Table 1 and Fig. 2 show the conditions of electroplating and the method for evaluation of whiskers which generate from electroplated tin films, respectively. The bath for electroplating was a solution of alkanol sulfonic acid for industrial use, and substrate was either rolled sheets of copper with weak cube orientation or a cast chromium plate with mirror-polished surface. In the following sentences, electroplated tin film is expressed as 'plated film' unless otherwise mentioned, and the thickness is 1 or 10 μm . Specimen-A (on copper) was kept in the ultra-high vacuum ($\sim 10^{-8} \text{ Pa}$)

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Table 1 Conditions of electroplating.

Tin plating	
Bath	Alkanol sulfonic acid (Ishihara Chemical Co., Ltd.)
Tin	AS-S15 (133 kg/m ³ -solution)
Acid	MS-A (100 kg/m ³ -solution)
Additive	HS-5 (30 × 10 ⁻³ m ³ /m ³ -solution)
Thickness	1 or 10 μm
Current density	5 × 10 ³ A/m ²
Anode	Rolled sheet of tin for Hull cell test (Yamamoto-MS Co., Tokyo)
Temperature	298 K
Cathode for tin plating	
Copper	Rolled sheet for Haring cell test (Yamamoto-MS)
Size (Cu)	10 mm (transverse direction) 25 mm (rolling direction) 300 μm (thickness)
Chromium	Mirror-polished cast plate (Kojundo Chemical Laboratory Co., Ltd.)
Size (Cr)	10 × 25 × 5 mm ³
Copper plating	
Bath	CuCN 80 kg/m ³ , KCN 15 kg/m ³ , KOH 200 kg/m ³
Thickness	1 μm
Current density	5 × 10 ³ A/m ²
Anode	Rolled sheet of copper for Haring cell test (Yamamoto-MS)

Fig. 2 Schematic illustration of experiment for evaluation of generation and growth of whisker.

chamber of an Auger electron spectrometer immediately after plating, and specimen-B was kept in air. Specimen-C (on copper) underwent the compression testing which indents a zirconium oxide ball of 1 mm in diameter with a load of 2.94 N. Specimen-D was a plated film peeled from the chromium substrate after a single-hole grid of molybdenum was glued on. Specimen-E was a peeled film which underwent the compression testing on a glass plate. Specimen-F, G

are double-layered films of tin (1 μm) and copper (1 μm), which were examined in the same ways as specimens-D and E.

A field emission Auger electron spectrometer (FE-AES) was used for observation of the surfaces of specimen-A, and a field emission electron probe microanalyzer (FE-EPMA) for surface and cross-sectional observation and elemental analysis. A part of the surface of specimen-A was etched by argon ion beam in the chamber of the FE-AES in order to remove the native oxide scale (~10 nm-thick), and the change in surface morphology was observed. A microtome was used in the sample preparation for cross-sectional observation and analysis, where rough sectioning was performed by glass knife, followed by sectioning with diamond knife (blade angle 45°, final feed 50 nm, sectioning speed 0.1 mm/s).

A microfocus X-ray diffractometer (wavelength $\lambda_{\text{CuK}\alpha} = 0.1542$ nm, specimen oscillation $\Delta x, \Delta y = 0.5$ mm) with two-dimensional detector was used for measuring residual stress of plated films. Strain tensor was calculated by measuring the distortion of diffraction intensities in reciprocal space, then, stress tensor was evaluated³⁻⁶⁾ by setting Young's modulus and Poisson ratio as $E = 41.4$ GPa and $\nu = 0.3$, respectively. The diffraction peak of (620)_{Sn} ($2\theta = 113.34^\circ$), which showed the weakest texture, was used for the above calculation.

3. Experimental Results

3.1 Formation of whiskers from electroplated tin films on copper substrate

Figure 3 shows secondary electron images of whiskers (specimen-A, B 5.2 Ms) which grew on the rolled surface. While the unetched area of specimen-A (Fig. 3(b)) had the most and the longest whiskers among the three areas, those on specimen-B (Fig. 3(c)) were ~10 μm at the longest. No

Fig. 3 Secondary electron images of tin plating (1 μm) on rolled surface after 5.18 Ms. (a) Specimen-A (etched), (b) Specimen-A, (c) Specimen-B.

Fig. 4 Secondary electron images of tin plating (1 μm) on cut surface of specimen-A. (a) 0.346 Ms, (b) 0.605 Ms, (c) 5.18 Ms

whiskers but only nodules as Fig. 1(d) were observed on the etched area of specimen-A (Fig. 3(a)). Here, the diameter of whiskers and nodules is $\sim 1\ \mu\text{m}$, which is almost the same as that of the grain size of tin.

Figure 4 shows secondary electron images of whiskers which formed from the cut surface of specimen-A. In Fig. 4, the whisker denoted by (i) stands straight at 0.346 Ms (in Fig. 4(a)), then, it kinks at its root (0.605 Ms), showing no meaningful change at 5.18 Ms. The whisker (ii) in Fig. 4 begins to grow at its root after kinking, and the diameter of the root after kinking was larger than that observed in Fig. 4(a). The whisker (iii) in Fig. 4 clearly shows growth at its root and kinking in the same manner as the whiskers (i) and (ii).

3.2 Properties of electroplated film, interface and whisker

Figure 5 shows cross-sectional area analysis of the rolled surface of specimen-B. Copper-tin intermetallic compound developed at the interface between the plated film and the substrate, identified as Cu_6Sn_5 by the X-ray diffraction pattern obtained on the plated surface.

Figure 6 shows changes in residual stress of the plated films (specimen-B). The residual stress was negative or compressive, and the absolute value increases as Cu_6Sn_5 develops in the case of 1 μm -thick. However, the 10 μm -thick specimen did not show any meaningful change. Formation of whiskers was observed at around 0.26 Ms after plating in the case of specimen-B (1 μm). The time corresponds to the point where Cu_6Sn_5 began to be identified in X-ray diffraction patterns, and the residual stress exceeded 20–30 MPa.

Figure 7 shows changes in orientation of the plated films and the whiskers of specimen-B. Figures 7(a), 7(b) are the results for the surface of a kinked whisker, showing that the change in orientation is less than 2° , i.e., the whisker is a single crystal despite the kinked shape. Figure 7(d) shows the

Fig. 5 Cross-sectional area analysis of tin plating (1 μm) on rolled surface of specimen-A (1.21 Ms) obtained by EPMA. (a) Sn-L α , (b) Cu-K α

Fig. 6 Residual stress of specimen-B obtained by X-ray diffraction.

Fig. 7 Crystal orientation map of whiskers obtained by EBSD. (a) Image quality (Surface), (b) Crystal orientation map of (a), (c) Secondary electron image, (d) Crystal orientation map of the kinked area in (c), (e) Crystal orientation map of the straight area in (c)

Fig. 8 Change of tin plating around indentation after compression test for 0.605 Ms (specimen-C). (a) Secondary electron image (1 μm , surface), (b) Secondary electron image (10 μm , surface), (c) Cross-sectional backscattered electron image of (b), (d) Grain boundary map of (c)

cross-sectional change in orientation of the indicated area (left) of Fig. 7(c). Three grain boundaries were observed between the tip of the whisker and its root grain, where the change in orientation is $\sim 5^\circ$. Figure 7(e) shows the cross-sectional change in orientation of the indicated area (right) in Fig. 7(c). In this case, the region is a single crystal with no obvious grain boundary, and the orientation spread was less than 2° .

3.3 Deformation by external force and formation of whiskers

Figure 8 shows the surface and cross-section of the indentations introduced by the compression testing (specimen-C, 0.605 Ms). Although many curved whiskers were found around the indentation in Fig. 8(a) (1 μm), Fig. 8(b) (10 μm) shows few whiskers even around the indentation. In the case of the 10 μm -thick sample, neither whiskers nor nodules were found on the surface far from the indentation (specimen-B). Figure 8(c) shows the cross-sectional backscattered electron image from the center of Fig. 8(b). Plastic flow of the plated film occurred as a result of indenting with a zirconium oxide ball, and an upheaval is formed which corresponds to the extruded volume. Figure 8(d) is a cross-sectional grain boundary map of this region obtained by EBSD. The interface between the plated film and the substrate shows Cu_6Sn_5 similar to that observed in Fig. 5, whose thickness is $\sim 1 \mu\text{m}$. While the original microstructure of the plated film consisted of columnar grains with diameter of $\sim 5 \mu\text{m}$, the raised area showed coarsened grains with small-angle boundaries whose change in orientation was less than 15° .

Figure 9 shows secondary electron images of the plated films (specimen-D, E, F, G) peeled from the polished chromium substrate. In the case of peeled tin film (1 μm), no whiskers were observed either after keeping in air (specimen-D, Fig. 9(a)), or after the compression testing for 0.605 Ms (specimen-E, Fig. 9(b)). On the other hand, nodules formed on the double-layered film (Sn 1 μm + Cu 1 μm) after keeping in air for 0.605 Ms (specimen-F, Fig. 9(c)). Although compression testing increased the number of nodules (specimen-G, Fig. 9(d)), no needle-like growth was observed.

Fig. 9 Secondary electron images of the surface of peeled tin film (1 μm) after 0.605 Ms. (a) Specimen-D, (b) Specimen-E, (c) Specimen-F, (d) Specimen-G

4. Discussion

4.1 Mechanism of generation and growth of whiskers

Figure 3 shows that surfaces not covered with native oxide scale (specimen-A) bear many nodules, and surfaces kept in vacuum (specimen-A) form longer and more whiskers compared with the one kept being oxidized in air (specimen-B). From this point, the native oxide scale itself is supposed to suppress formation and growth of whiskers, and once growth of a whisker is initiated, the non-oxidizing environment increases its speed. It is also considered that formation of many nodules decreases the number of long whiskers, and nonuniformity or especially local fragility of native oxide scale brings about less nodules and rapid growth of particular whiskers. Here, "fragility" corresponds to lower surface energy or thinner oxide film which can fracture rather easily, and the effect of this property is discussed in 4.3.

Since length of whiskers can exceed 100 μm , a whisker is not thought to be formed as a result of compression and prominence of a tin grain, whose diameter and height are $\sim 1 \mu\text{m}$, but a whisker is a result of continuous extrusion from the surface by supply of tin atoms from the grains which surround a particular grain. The migration or diffusion of tin atoms means a supply of tin atoms from the areas where free energy is high and tin atoms are unstable into the more stable grains. Here, free energy of interest is the term originating from residual stress shown in Fig. 6. Residual stress increases as Cu_6Sn_5 (Fig. 5) grows, and the correlation is considered to be based on the volume change and crystallographic coherency. The former is caused by the difference in densities of tin and Cu_6Sn_5 (macroscopic stress), and the latter is generally based on the crystal structures and the orientation relationships (microscopic stress). That is, these factors can form spatially nonuniform stress field, and tin atoms are thought to migrate from the highly strained grains into the moderate ones, where growth of whiskers is observed.

From the point that crystal orientations of tin on one side of a Cu_6Sn_5 grain is different from that on the other side,

Cu_6Sn_5 is considered to nucleate on the lines where grain boundaries of tin meet the interface between tin plated film and copper substrate, then grow along the grain boundaries of tin. If a grain of Cu_6Sn_5 is crystallographically coherent with a tin grain to lower the interface energy, a strain field is formed in this side of the tin grain. Since the other interface should be incoherent, its strain is supposed to be smaller concerning crystallographic coherency. Although formation of Cu_6Sn_5 may cause gradients in free energy, cross sections made by diamond knife showed quite diffuse EBSD patterns at Cu_6Sn_5 whose crystal orientation could not be determined. The more appropriate sample preparation for EBSD measurement as well as TEM analysis on tin and Cu_6Sn_5 are to be performed in a future work.

Here, mass transfer of tin required for growth of whiskers is discussed. Generally, the diffusion modes of atoms⁷⁾ are lattice diffusion where vacancies are the media, grain boundary diffusion, surface diffusion and dislocation diffusion. The speed in the latter three modes is usually higher than that of lattice diffusion by a few orders of magnitude. The extrapolated self-diffusion coefficient of a tin single crystal^{8–10)} at 298 K is $D_{\text{Sn self}}(298 \text{ K}) \sim 10^{-22} \text{ m}^2/\text{s}$. Compared with the impurity diffusion coefficient of copper in a tin single crystal¹¹⁾ $D_{\text{Cu in Sn}}(298 \text{ K}) \sim 10^{-13} \text{ m}^2/\text{s}$, lattice diffusion of tin is extremely slow. The fixed-point observation of whiskers (Fig. 4) shows the growth speed of whiskers is $\sim 10^{-1} \mu\text{m}/\text{ks}$, therefore, the supply rate or diffusion flux of tin atoms needs to be $\sim 10^{-6} \text{ mol}/\text{m}^2 \text{ s}$. Here, the root grain of a whisker is simplified to be a cylinder whose diameter and height are $1 \mu\text{m}$, and tin atoms are assumed to be supplied through the side surface. If a gradient of stress or strain causes migration of tin atoms and growth of whiskers, it is difficult to discuss the detailed kinetics of the system by considering the diffusion coefficient which is related to the gradient of concentration of tin. However, grain boundaries, surface and dislocations, as well as vacancies, should play important roles in diffusion rate of tin.

Figure 10 shows a schematic illustration of growth of a whisker by supply of tin atoms according to the above mechanism. When tin atoms migrate into the root grain of a whisker, vacancies are occupied by tin atoms, and the concentration of vacancy temporarily decreases. Since the concentration of vacancy tends to recover to the thermal equilibrium value, macroscopic expansion to the surface occurs. In an opposite manner, the volume of the grain, which supplies the root grain of the whisker with tin atoms, decreases because of an increase in vacancies and subsequent recovery to the thermal equilibrium state. The process is considered to last until the residual stress of tin is relieved or tin around the whisker disappears. However, the continued increase of compressive residual stress (Fig. 6) suggests that release of macroscopic stress by diffusion of tin does not work effectively, or that meaningful macroscopic stress does not exist.

On the other hand, if microscopic stress due to crystallographic relationship between tin and Cu_6Sn_5 is dominant in the measured residual stress, then residual stress will continue to be detected and whiskers to grow as long as coherent interfaces and paths for diffusion of tin atoms exist. In either case, growth of Cu_6Sn_5 along grain boundaries of tin

Fig. 10 Schematic illustration of generation and growth of whisker. (a) Formation of Cu_6Sn_5 and inhomogeneous compressive stress, (b) Migration of Sn atoms, (c) Generation and growth of whisker

is considered to bring about nonuniformity in strain field, diffusion of tin atoms into specific sites, and formation of whiskers where native oxide scale is locally thin. Since the state of oxidation on the surface of tin may depend on which crystallographic plane faces the surface, it is also important to take into account the effects of substrate, underlying plated film, current density during electroplating, bath, additives, resulting texture and surface morphology on generation and growth of whiskers.

Next, effect of existence of substrate and Cu_6Sn_5 on formation mode of whiskers is discussed. From Figs. 9(a), 9(b), neither nodules nor whiskers formed after compression testing on the peeled tin film. The multi-layered plated film of copper and tin showed nodules when it was kept in air (Fig. 9(c)). Although more nodules were observed after compression testing (Fig. 9(d)), they did not grow to be whiskers. These phenomena mean that growth of whiskers need residual stress due to constraint by rigid substrate. That is, if the plated film can freely deform itself and the strain caused by formation of Cu_6Sn_5 can be released, the driving force which changes nodules into whiskers, or the driving force for tin atoms migration, does not develop in the system.

From the above results and discussion, suppression of whiskers could be effectively accomplished by uniform formation of intermetallic compounds as Cu_6Sn_5 , formation of uniformly fragile native oxide scale and resulting many nodules. Introduction of another phase, which assists in the release of strain in tin, is also an effective measure. Lead is considered to have preferable effects on these three aspects, as discussed in the pervious report.¹²⁾

4.2 Mechanism of kinking of whiskers

As observed in Fig. 4, some of the whiskers stop growing after kinking at their roots. In addition, meaningful change in crystal orientation was not observed (Fig. 7(b), 7(e)) at most

Fig. 11 Schematic illustration of kinking of whisker at the root. (a) Straight growth of whisker, (b) Change of crystal orientation at the root grain, (c) Unbalanced growth and resulting kink at the root

of the kinked areas. Even when a change in orientation was observed, the areas showed small angle grain boundaries (Fig. 7(d)) where orientation changed by $\sim 5^\circ$. As mentioned in 4, growth of a whisker is the expansion of its root grain, and the crystal orientation of the whisker, the root grain and the new volume should be identical from the viewpoint of minimization of interfacial energy. Here, Fig. 8(d) shows that deformation of tin causes recovery, recrystallization and orientational change at room temperature, and crystal orientation can be changed by grain growth. That is, when a grain boundary is formed between a whisker and the root grain by its orientational change due to growth of Cu₆Sn₅ or grain growth of tin, lowering grain boundary energy is thought to occur which takes full advantage of growth of the whisker.

Figure 11 shows schematic illustration of the above phenomenon. Suppose the initial state of Fig. 11(a) and another state of Fig. 11(b) where orientational change has occurred in the root grain caused by recovery, recrystallization or grain growth. If the whisker which has already been formed is rotated by formation of the wedge-like volumes between the whisker and the root grain (Fig. 11(c)), kinking at the root (Fig. 4), appearance of a new volume after kinking whose size is different from the previous one (whisker (ii) in Fig. 4), and small changes in orientation (Fig. 7) can be well explained. Continuous formation of the infinitesimal wedge-like volumes, which mechanically rotate the overlying whisker, is observed as the asymmetric growth of the whisker with respect to its central axis. According to this mechanism, a curved whisker should be observed when the orientation of the root grain continuously changes. The

Fig. 12 Energy change by growth of whisker. (a) Before growth, (b) After growth by Δd , (c) $\eta = 0.2$, (d) $\eta = 0.3$, (e) $\eta = 0.4$.

curved whiskers in Fig. 8(a) could be explained as a result of the orientational change in the root grain due to continuous deformation, recovery and recrystallization during compression testing. Here, the whiskers in Fig. 4 are on the cut edge of the substrate, and the direction of gravity is from this side of the paper face toward the other side. Since the whiskers (i), (ii), (iii) kink toward this side, kinking of whiskers is not a plastic deformation or activity of dislocations induced by gravity.

4.3 Change in free energy by growth of whiskers

Here, change in free energy is derived regarding the process of growth of whiskers discussed in 4. Figures 12(a), 12(b) show schematic illustration of the growth of a whisker by the length Δd . Supply rate of tin is not taken into account in this model, but a static treatment is discussed which deals with the change in free energy with respect to the increase in vacancy. When the root grain of the whisker is assumed to be a column (radius r , height d), the number of tin atoms in the grain N is given by eq. (1) using density of tin ρ , atomic mass M and Avogadro constant N_A .

$$N = \frac{\rho N_A}{M} \pi r^2 d \quad (1)$$

The number of vacancies in the root grain, n , and that introduced by the growth of the whisker, Δn , are given by eqs. (2) and (3), respectively, where c_v is the concentration of vacancies and α is the coefficient which means the increase in vacancy.

$$n = c_v N \quad (2)$$

$$\Delta n = \alpha N \quad (3)$$

Elongation of the whisker, Δd , is related to the increase in vacancies, Δn , and the relation is given by eq. (4), where v_v is the volume of a vacancy.

$$\begin{aligned}\pi r^2 \Delta d &= v_v \Delta n \\ \Delta d &= \frac{v_v N}{\pi r^2} \alpha\end{aligned}\quad (4)$$

Growth of the whisker is accompanied by the formation of new surface, and the increase in surface energy, ΔG_s (surface), is given by eq. (5), where γ is the surface energy of a unit area.

$$\begin{aligned}\Delta G_s &= 2\pi r \Delta d \gamma \\ &= \frac{2v_v N \gamma}{r} \alpha\end{aligned}\quad (5)$$

When enthalpy for forming a vacancy and corresponding change in entropy are given by Δh_v and Δs_v , respectively, change in free energy for forming a vacancy, Δg_v , and that of the system, ΔG_v (vacancy), are expressed as follows.

$$\Delta g_v = \Delta h_v - T \Delta s_v \quad (6)$$

$$\begin{aligned}\Delta G_v &= \Delta n \Delta g_v \\ &= N (\Delta h_v - T \Delta s_v) \alpha\end{aligned}\quad (7)$$

Introduction of vacancies increases entropy of configuration in terms of statistical mechanics. The corresponding change in free energy, ΔG_c (configuration), is given by eq. (11), according to the Boltzmann formula.

$$\begin{aligned}\Delta G_c &= -T \Delta S_c \\ &= -T k_B \left[\ln \frac{(N+n+\Delta n)!}{N!(n+\Delta n)!} - \ln \frac{(N+n)!}{N!n!} \right]\end{aligned}\quad (8)$$

$$\begin{aligned}&\simeq -k_B T \left[(N+n) \ln \left(1 + \frac{\Delta n}{N+n} \right) \right. \\ &\quad \left. - n \ln \left(1 + \frac{\Delta n}{n} \right) - \Delta n \ln \frac{n+\Delta n}{N} \right]\end{aligned}\quad (9)$$

$$\simeq -k_B T \left[\Delta n \left(1 - \ln \frac{n+\Delta n}{N} \right) - n \ln \left(1 + \frac{\Delta n}{n} \right) \right] \quad (10)$$

$$= -N k_B T \left\{ \alpha [1 - \ln(c_v + \alpha)] - c_v \ln \left(1 + \frac{\alpha}{c_v} \right) \right\} \quad (11)$$

Here, the Stirling's approximation is used in the transformation from eq. (8) to eq. (9), and that from eq. (9) to eq. (10) is performed by taking into account the first order of the infinitesimal terms in the Taylor expansion of the first term in the square brackets. The change in free energy of the system caused by growth of the whisker is given by eq. (12), using eqs. (5), (7) and (11).

$$\Delta G = \Delta G_s + \Delta G_v + \Delta G_c \quad (12)$$

In the calculation of the change in free energy, temperature T is 298 K, the size of the root grain of the whisker is given as $r = 0.5 \mu\text{m}$, $d = 1 \mu\text{m}$, and the surface energy γ is 1 J/m^2 . The volume of a vacancy v_v is assumed to be the same as that of a tin atom ($2.7 \times 10^{-2} \text{ nm}^3$). Enthalpy Δh_v and entropy Δs_v required for making a vacancy are expressed as eqs. (13) and (14), respectively, using the elementary charge e and Boltzmann constant k_B as units.

$$\Delta h_v = \eta e \quad (13)$$

$$\Delta s_v = \sigma k_B \quad (14)$$

From these formulas and values, eqs. (5), (7) and (11) become (15), (16), (17), respectively.

$$\Delta G_s = 3.1 \times 10^{-12} \alpha \quad (15)$$

$$\Delta G_v = 4.6 \times 10^{-9} (\eta - 2.6 \times 10^{-2} \sigma) \alpha \quad (16)$$

$$\begin{aligned}\Delta G_c &= -1.2 \times 10^{-10} \left\{ \alpha [1 - \ln(c_v + \alpha)] \right. \\ &\quad \left. - c_v \ln \left(1 + \frac{\alpha}{c_v} \right) \right\}\end{aligned}\quad (17)$$

Here, η and σ in eq. (16) are known to be $\sim 10^{-1}$ – 10^0 .^{13,14} Since the second term in the parentheses is negligible compared to the first term, σ is assumed to be 0 in the following calculation.

Figures 12(c)–12(e) show the calculated changes in free energy ΔG (eq. (12)) with respect to c_v and α , where η is a parameter. In the contour plots of Figs. 12(c)–12(e), $\log_{10} |\Delta G|$ is used and the boundaries at which $\Delta G = 0$ are shown by the dashed line. Growth of the whisker should occur in the region of $\Delta G < 0$, which enlarges as η decreases. Increase in the absolute value of ΔG in this region for smaller η means that the system is remarkably stabilized by growth of the whisker when Δh_v is small. From these results, decrease of enthalpy required for the formation of a vacancy is thought to promote growth of whiskers.

Since c_v at the upper-left end of the dashed line in Figs. 12(c)–12(e) shows the concentration of vacancy at thermal equilibrium, the system is stabilized by formation of certain amount of vacancies and resulting growth of whiskers when c_v decreases as a result of diffusion of tin. That is, the whisker grows for stabilization of the system as long as the root grain is supplied with tin atoms and vacancies keep decreasing. If an incubation period is required for the increase in the concentration of vacancies, c_v keeps decreasing as tin atoms diffuse into the root grain. In this case, ΔG which means the degree of stability of the system is minimized, or the system is most stabilized, by taking an appropriately large α compared with the case of infinitesimal α in which the whisker grows as soon as the concentration of vacancies decreases. This corresponds to the transition of the system during the incubation period into the lower left brightest region in Figs. 12(c)–12(e) where ΔG is lowest.

The increase in the surface energy caused by growth of the whisker is considered to be negligible since eq. (15) is smaller than eq. (16) by order of three. However, since the surface of the whisker is covered with native oxide scale, additional free energy should be taken into account which describes deformation and fracture of oxide film. The additional term can be discussed by γ in eq. (5) which corresponds to the tension of the native oxide scale. Then, the change of free energy with respect to the increase in vacancies or α is given by eq. (18)

$$\left. \frac{\partial(\Delta G)}{\partial \alpha} \right|_{\alpha=0} = \frac{2v_v N \gamma}{r} + N (\Delta h_v - T \Delta s_v) + N k_B T \ln c_v \quad (18)$$

The condition that eq. (18) becomes negative, i.e., that free energy decreases by introducing vacancies, is given by eq. (19).

$$\varepsilon < \exp \left(-\frac{2v_v \gamma}{r k_B T} \right) \quad (19)$$

Here, ε is a ratio of c_v and concentration of vacancies at

thermal equilibrium, defined by eq. (20).

$$c_v = \varepsilon \exp\left(-\frac{\Delta g_v}{k_B T}\right) \quad (20)$$

From eq. (19), ε is required to be smaller for larger γ in order to stabilize the system by formation of vacancies or growth of the whisker. Since the region where the concentration of vacancies is extremely low is unstable in the first place, the incoming flow of tin atoms is considered to cease, then, other regions begin to accept tin atoms where whiskers can grow more easily.

5. Summary

In this paper, generation and growth of whiskers and nodules were studied for electroplated tin films on copper substrate, those peeled from chromium substrate and multi-layered films of tin and copper. Mechanism of generation and growth of whiskers was proposed by considering the effect of native oxide scale and external stress, evolution of morphology of whiskers and residual stress, as well as the crystallographic relationships between the whiskers and the root grains, then, the process was discussed from the viewpoint of diffusion of tin atoms. The results are summarized as follows.

- (1) No whiskers but many nodules were found on the surface of the plated film in vacuum after etching by argon ion beam. The number and the length of whiskers on the surface of the plated film kept in vacuum immediately after electroplating exceed those kept in air. From these results, native oxide scale is considered to suppress generation of nodules and growth of whiskers.
- (2) Although whiskers kink at the roots, misorientation between the whisker and the root grain was at most 5° . Kinking of a whisker is considered to be the result of an asymmetric growth of the whisker caused by the misorientation between the whisker and the root grain.
- (3) When an electroplated tin film is deformed, recovery, recrystallization, rotation of crystal orientation and grain growth occurred at room temperature. Rotation of crystal orientation in root grains is attributed to these phenomena, and curved whiskers are considered to develop when the orientations continuously change at the root grain.
- (4) Residual stress of tin increased as Cu_6Sn_5 grew, and whiskers began to be observed when the stress exceeded ~ 20 MPa. Residual stress is supposedly due to coherency between tin and Cu_6Sn_5 , as well as the change in volume caused by growth of Cu_6Sn_5 .
- (5) Nonuniformity of residual stress fields is considered to induce diffusion which follows the gradient of strain. Although concentration of vacancies temporarily decreases in areas into which tin atoms diffuse, it will approach the thermally equilibrated value to generate a new volume and grow whiskers.
- (6) Discussions of the change in free energy, which takes concentration of vacancy and stability of native oxide scale into account, show the conditions which balance fracture of native oxide scale and growth of whisker. This suggests that diffusion of tin atoms which causes growth of whiskers is suppressed by formation of stable native oxide scale.

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