Microstructure of Sn-Ag Alloys Electrodeposited from Pyrophosphate-Iodide Solutions[†]

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Tin-silver (Sn-Ag) alloys, which are considered to be suitable for use as Pb-free solder, were made by an electrodeposition method. A newly developed Sn-Ag alloy electroplating bath containing pyrophosphate and iodide as the complexing agents of Sn and Ag was used. The composition, morphology, phases and microstructure of electrodeposited Sn-Ag alloys were studied. The results are summarized as follows: (1) A good relationship was observed between the morphologies of the electrodeposited Sn-Ag alloys and their compositions. (2) The electrodeposited Sn-Ag alloys ranging in Ag content from 5 to 75 at% exhibited two phases (β -Sn and an intermetallic compound), and were composed of grains of submicron-order diameter. (3) The phase diagram of the electrodeposited Sn-Ag alloys resemble the equilibrium phase diagram of the Sn-Ag alloys.

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I. Introduction

Sn-Ag alloys and Sn-Ag type alloys are considered to be suitable for use as Pb-free solder from the viewpoints of mechanical, soldering, creep and thermal cyclic fatigue characteristics. Accordingly, many reports have recently been published regarding Sn-Ag alloys produced by casting⁽¹⁾⁻⁽⁶⁾. However, there have been very few reports on the electrodeposition of Sn-Ag alloys or Sn-Ag type alloys for use as materials for solder plating. Several reports on the electrodeposition of Ag-Sn alloys with high Ag concentration for use as a plating material instead of Ag plating have been published; in these reports, electrodeposition baths containing cyanide compounds which are toxic to humans were used⁽⁷⁾⁻⁽¹⁰⁾.

We studied the production of Sn-Ag alloys using Pb-free and cyanide-free electrodeposition, in which a pyrophosphate-iodide bath was used as a Sn-Ag plating bath and analyzed the electrodeposition mechanism and other characteristics⁽¹¹⁾⁽¹²⁾.

Watanabe *et al.* reported that in electrodeposited alloys, nonequilibrium phases which do not exist in the equilibrium phase diagram sometimes appear, and that the alloys with the same composition have a structural phase which is different from that which exists in the equilibrium phase diagram⁽¹³⁾. Electrodeposited Sn-Ag alloys produced in cyanide baths were known to have structural phases different from those in the equilibrium phase diagrams⁽⁸⁾.

The physical properties of metals or alloys are greatly influenced by their structural phases and microstructures.

Melting point, wettability, elongation and other properties of electrodeposited Sn-Ag alloys are very important for use as solder plating and these properties are affected by the structural phases and microstructure.

In this study, we investigated the composition, surface morphology, structural phase and microstructure of the Sn-Ag alloy plating films produced using a pyrophosphate-iodide bath which we developed. The structural phases were investigated taking into account the equilibrium phase diagram.

II. Experimental Method

Table 1 shows the composition of plating baths used in the study. To produce Sn-Ag alloy films of various compositions, we prepared two baths (bath A and bath B) with different Sn/Ag compositions. As the cathode, a pure Cu plate (aperture area: $2 \times 10^{-4} \text{ m}^2$) which was mirror-finished by electrolytic polishing in a solution of phosphoric acid after heat treatment at 600°C for 1 h. A platinum plate was used as the anode. Electrodeposition was performed at room temperature ($25 \pm 2^\circ\text{C}$) without agitation, varying the current density from 10–100 Am^{-2} with a constant charge of 13 C. The surface morphology of the electrodeposited films was observed using a scanning

Table 1 Bath composition (mol/L).

Reagents	Bath A	Bath B
$\text{K}_4\text{P}_2\text{O}_7$	0.54	0.54
KI	2.0	2.0
$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	0.18	0.195
AgI	0.02	0.005

pH=8.9

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electron microscope (SEM: JSM-6100, JEOL Ltd.), and the crystal structures of the films were analyzed by a thin-

film X-ray diffraction method (RAD-1C, Rigaku Denki). The cross-sectional structure of the electrodeposited films was observed with a transmission electron microscope (TEM: JEM-2000FX, JEOL Ltd.); thin samples were prepared using a microtome. Cross-sectional composition analysis of the thin samples was conducted using EDS attached to the TEM. The diameter of the probe was 10nm. Film composition was analyzed using an energy-dispersive X-ray analyzer (EDX) attached to the SEM. EDX analysis was conducted by multi-point analysis with ZAF correction. High-frequency inductively coupled plasma analysis (ICP: ICPS-5000, Shimadzu Corp.) was also performed; the results of the ICP analysis were almost identical to those of the EDS analysis.

Fig. 1 Relationship between current density and composition of electrodeposited films.

III. Experimental Results and Discussion

1. Composition of electrodeposited films

Figure 1 shows the relationship between current density and composition for the electrodeposited films. The

Fig. 2 Morphology of Sn-Ag alloy films electrodeposited from bath A and bath B at various current densities.

(a) 6 at% Ag (70 Am^{-2} from bath B), (b) 7 at% Ag (60 Am^{-2} from bath B), (c) 9 at% Ag (40 Am^{-2} from bath B), (d) 10 at% Ag (30 Am^{-2} from bath B), (e) 11 at% Ag (20 Am^{-2} from bath B), (f) 21 at% Ag (10 Am^{-2} from bath B), (g) 22 at% Ag (100 Am^{-2} from bath A), (h) 27 at% Ag (50 Am^{-2} from bath A), (i) 30 at% Ag (40 Am^{-2} from bath A), (j) 42 at% Ag (30 Am^{-2} from bath A), (k) 70 at% Ag (20 Am^{-2} from bath A) and (l) 75 at% Ag (10 Am^{-2} from bath A).

figure shows that for the current densities ranging from $10\text{--}100\text{ A m}^{-2}$, the films with 20–75 at% Ag were produced in bath A, and the films with 5–21 at% Ag in bath B. Thus, the Sn-Ag alloys with a wide range of Ag content (5–75 at%) were produced. The content of Ag, whose deposition potential is higher than that of $\text{Sn}^{(9)(10)}$, tended to decrease with increasing current density. This result indicates that Sn-Ag alloy plating is of a normal codeposition type⁽¹⁴⁾.

2. Surface morphology of electrodeposited films

Figure 2 shows scanning electron micrographs of electrodeposited films produced in bath A and bath B at different current densities. As shown in Fig. 1, since the change in current density relates to a change in composition of the electrodeposited films, Fig. 2 indicates a correlation between the composition and their surface morphologies of the electrodeposited films. In the electrodeposited film with 6 at% Ag (a), irregular surface morphology was observed; with an increase in Ag content, the surface morphologies of the films became smoother (b)–(e), and the smoothest surface was obtained for the films with approximately 20 at% Ag (f) and (g). When the Ag content increases more (h), a geometrical pattern appears in the smooth morphology. With a further increase in Ag content (i)–(k), the area of this geometrical morphology increases and the degree of surface irregularity also increases. In the case of 75 at% Ag (l), the entire film surface exhibits the morphology with a geometrical pattern.

3. Structure of electrodeposited films

Figure 3 shows X-ray diffraction patterns of the electrodeposited films of various compositions produced in baths A and B at different current densities. Sharp diffraction peaks were observed in all the patterns, indicating that the electrodeposited films have a crystalline structure. With respect to the relationship between the composition and phase of the electrodeposited films, strong diffraction peaks attributable to the β -Sn phase and the weak peaks attributable to intermetallic compound (ϵ or ζ phase) were observed in the films with low Ag content (a)–(d); with an increase in Ag content, the diffraction peaks for the β -Sn phase became weaker and those for the intermetallic compound (ϵ or ζ phase) became stronger (e)–(l). For the electrodeposited film with approximately 75 at% Ag (j), the diffraction peaks for β -Sn phase disappeared and only those for the intermetallic compound (ϵ or ζ phase) were observed.

In this study, whether the diffraction peaks attributable to the intermetallic compound correspond to the ϵ phase (Ag_3Sn) or the ζ phase (Ag_4Sn) is not clear, because the diffraction angles, i.e., the interplanar spacings, of the ϵ and ζ phases, are similar to each other⁽¹⁵⁾⁽¹⁶⁾.

Therefore, we determined the relationship between the diffraction angle of a peak with the largest intensity (diffraction angle of around 40 degrees) among the diffraction peaks attributable to the intermetallic compound and the Ag content of the films, as shown in Fig. 4. In this figure, the diffraction angles (2θ) are converted

Fig. 3 X-ray diffraction patterns for Sn-Ag alloy films having various compositions.

(a) 5 at% Ag, (b) 6 at% Ag, (c) 7 at% Ag, (d) 10 at% Ag, (e) 21 at% Ag, (f) 22 at% Ag, (g) 30 at% Ag, (h) 42 at% Ag, (i) 70 at% Ag and (j) 75 at% Ag

Fig. 4 The relationship between the interplanar spacing and composition of Sn-Ag films.

to the interplanar spacings (d). The crystal structures of ϵ and ζ phase which we used are orthorhombic ($a=5.9680$, $b=4.7802$, $c=5.1843$)⁽¹⁵⁾ and hexagonal ($a=2.966$, $c=4.782$)⁽¹⁶⁾, respectively. Horizontal lines of 0.22746 nm and 0.22787 nm shown in Fig. 4 indicate the interplanar spacing of (211) and (012) planes for the ϵ phase (Ag_3Sn) as described in the JCPDS card⁽¹⁵⁾. A horizontal line of

0.2263 nm indicates the interplanar spacing of (101) planes for the ζ phase (Ag_4Sn) as described in the JCPDS card⁽¹⁶⁾. From Fig. 4, it can be seen that when the Ag content is around 20 at%, the interplanar spacing is close to that of (211) or (021) planes of the ε phase, and when the Ag content exceeds 20 at%, the interplanar spacing approached that of (101) planes of the ζ phase. Thus, we speculate that with an increase in Ag content, either the lattice constant of ε phase continuously approaches the lattice constant of ζ phase, or both the ε and ζ phases are simultaneously present. However, since the d value is close to the interplanar spacing of (211) or (021) planes of the ε phase, a further study is required to identify the nature of the intermetallic compound in electrodeposited films.

4. Cross-sectional structure

Figure 5 shows transmission electron micrographs of the cross-sectional structures of the electrodeposited Sn–Ag films of various compositions, and electron diffraction patterns for the central area of the films. The aperture size of the selecting area is 0.792 μm in diameter. Traces of damage were observed on these micrographs. The damages were introduced at the time of preparation of the TEM samples with a microtome. In particular, for the film with an Ag content of approximately 75 at% (f), most of the film was damaged because it was fragile. However, no layered structure in the direction of thickness⁽¹⁷⁾ is observed in any of the films, and the electrodeposited films are uniformly produced on the Cu substrates. In addition, as exhibited by the results of X-ray

Fig. 5 Transmission electron micrographs showing a cross-sectional structure of the electrodeposited Sn–Ag alloy films having various compositions (above), and electron diffraction patterns at center area of the films (below).
(a) 7 at% Ag, (b) 11 at% Ag, (c) 21 at% Ag, (d) 22 at% Ag, (e) 27 at% Ag and (f) 75 at% Ag.

Fig. 6 (a) Enlarged picture of Fig. 5(c). (b') and (c') are the EDS analysis charts of the position (b) and (c) in Fig. 6(a).

diffraction analysis, the electron diffraction patterns show that the electrodeposited films consist of a β -Sn phase and an intermetallic compound phase, and the film with 75 at% Ag shows a diffraction pattern attributable only to the intermetallic compound. Figure 6 is an enlarged TEM photograph of Sn-Ag film shown in Fig. 5(c). The film grows in the direction from right to left. The results of cross-sectional analysis of the compositions of the bright crystal (b) and the dark crystal (c) in (a) are shown on the right-hand side of the figure as (b') and (c'). The Cu peaks observed in (b') and (c') originated from the Cu mesh on which thin film samples were placed. From Fig. 6(a), we can see that the crystals forming this film are of submicron size. The results of composition analysis show that crystal (b) contain about 1 at% Ag and crystal (c) contain about 70 at% Ag. Therefore, it is considered that crystal (b) consist of β -Sn, and crystal (c) consists of intermetallic compound (ϵ or ζ). Figure 7 shows an enlarged image of Fig. 5(c) ((a): bright-field image, (b): an electron diffraction pattern of central area of (a), (c): a dark-field image of (a) from β -Sn (200) spot shown in (b)). This figure also shows that the film consists of submicron-sized crystal grains. Dark-field images from the spot of intermetallic compound phase also showed the same result. Composition analysis by EDS and observation using dark-field images for other samples also demonstrated that the electrodeposited alloy films with 5–75 at% Ag produced in this experiment consisted of submicron-sized crystal grains of β -Sn and intermetallic compounds.

5. Phase diagram of electrodeposited Sn-Ag alloy films

Figure 8 shows the relationship between the composi-

Fig. 7 Enlarged picture of Fig. 5(c). (a) a bright-field image, (b) an electron diffraction pattern of central area of (a) and (c) a dark-field image of (a) from the β -Sn (200) spot shown in (b).

tion and the phase of the electrodeposited Sn-Ag alloy films, obtained from the X-ray diffraction and electron diffraction patterns. For comparison, the equilibrium phase diagram for the Sn-Ag alloys is shown in Fig. 8(a). The Ag content of the electrodeposited Sn-Ag alloys produced in this study varies between 5 and 75 at%. When the Ag content is around 75 at%, the alloy consists only

Fig. 8 Comparison of phase diagram of electrodeposited Sn-Ag alloy with those of thermally equilibrium Sn-Ag alloy.
(a) Thermally equilibrium Sn-Ag alloy phase diagram and (b) Electrodeposited Sn-Ag alloy phase diagram.

of the intermetallic compound phase; when the Ag content is less than 75 at%, *i.e.*, the Sn content is 25 at% or more, the alloy consists of the β -Sn phase and the intermetallic compound phase. These findings suggest that the state diagram of the Sn-Ag alloys obtained in this study resembles the Sn-Ag alloy equilibrium phase diagram. The structures obtained in this study differ from those of the Sn-Ag alloy films produced in a cyanide bath⁽⁸⁾. It was known that as the cyanide bath was used for the electrodeposition of Sn-Ag alloys, Ag (α) phase exists in the range of Ag content from 0 to 50 at% and the ϵ phase did not appear (Ag contents ranging 0–50 at%: α and ζ phase exist, Ag contents ranging 50–70 at%: α , ζ and β phase exist, Ag contents ranging 70–100 at%: ζ , β phase exist). This is considered to be due to the difference in electrodeposition potential caused by the difference in the state of metallic ions in electrodeposition baths (cyanide complex ions in the cyanide bath and pyrophosphoric complex ions or iodide complex ions in the pyrophosphate-iodide bath), or due to the difference in the codeposition mechanisms. However, all the films of different compositions produced in this study exhibited a thermal equilibrium state. The Sn-Ag alloys produced in this study are expected to exhibit physical properties similar to the Sn-Ag alloys produced by casting.

6. Relationship between surface morphology and crystallographic structure

As shown in Fig. 2, the surface morphology of the electrodeposited films differs depending on the composition of the films. The degree of surface irregularity of the films with either low or high Ag contents is high; in contrast, the surface of films with an Ag content of around 20 at% is fairly smooth. As clarified by the results shown in Figs. 3 and 5, the electrodeposited alloy films with Ag contents ranging from 5 to less than 75 at% have a β -Sn and intermetallic compound biphasic structure and those with 75 at% Ag have a single intermetallic compound phase. Thus, when the Ag content is high, the percentage of the intermetallic compound phase in the film increases, indicating that the crystal growth of the intermetallic compound phase greatly affects the surface morphology of the electrodeposited films. Consequently, the films exhibited different surface morphologies depending on the crystal system of the intermetallic compound (the orthorhombic system for the ϵ phase and the hexagonal system for the ζ phase). On the other hand, when the Ag content is low, the percentage of the β -Sn phase increases; therefore, the crystal growth of the β -Sn phase (pyramidal quadratic system) greatly affects the surface morphology. When the Ag content is around 20 at% (*i.e.*, 80 at% Sn), the crystal growth of the β -Sn and intermetallic compound phases interfere with each other, resulting in the generation of finer crystal grains and the smooth surface morphology.

IV. Conclusions

Considering an application such as Pb-free soldering, we investigated the microstructure of electrodeposited Sn-Ag alloy films having an Ag content of 5–75 at% using a newly developed pyrophosphate-iodide bath, and reached the following conclusions.

(1) The surface morphology of electrodeposited films correlates with film composition; the films with Ag contents of about 20 at% (Sn content of 80 at%) had a fairly smooth surface, and films with Ag contents higher or lower than 20 at% had an irregular surface.

(2) Electrodeposited films with Ag contents of about 75 at% exhibited only an intermetallic compound phase (ϵ or ζ phase), and those with Ag contents of 5–75 at% exhibited the β -Sn and intermetallic compound (ϵ or ζ phase) biphasic structure. Diameters of the crystal grains are in the submicron range.

(3) The phase diagram of the electrodeposited Sn-Ag alloy films resembles the Sn-Ag equilibrium phase diagram.

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