Effects of Reflow Processing and Flux Residue on Ionic Migration of Lead-Free Solder Plating Using the Quartz Crystal Microbalance Method

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To investigate the ionic migration, quite a new measurement method has been developed by the authors, which enables real time monitoring of the growth process of ionic migration using a QCM (Quartz Crystal Microbalance). This research has focused on the QCM method to study the growth process of ionic migration in various types of lead-free solder plating and the effects of the reflow processing and flux residue of soldering processes. In addition, we investigated the anode dissolution characteristics of the elements in each type of solder alloy by measuring the current-potential curve in 0.1 kmol m⁻³ KNO₃ solution. When using Sn–3.5 mass%Ag solder plating, reflow processing segregates the stable compound Ag₅Sn layer and Sn layer. The Sn layer selectively promotes the anode dissolution reaction, increasing the occurrence of migration. When using Sn–9 mass%Zn solder plating, the Sn effectively prevents the excessive dissolution reaction of Zn. However, since reflow processing causes each element to separate out, reflow processing lessens the effectiveness of Sn, thus promoting the occurrence of migration. The flux processing of lead-free solders suppresses anode dissolution and effectively prevents the occurrence of migration. However, with Sn–9 mass%Zn, the lowered adhesion between the flux film and the electrodes is a factor in speeding the growth of migration.

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1. Introduction

Ionic migration(hereafter, “migration”) occurs when moisture adheres to the gap between electrodes and voltage is applied to the metallic electrodes. Metallic dissolution is generated at the anode, and these metallic ions migrate to the cathode and form metallic deposits. As this process is repeated, short circuits form. The corrosion mechanism of alloys such as solder in particular is quite complex, affected by a variety of factors such as the potential for forming surface oxide film, the adhesive strength of that film, the anode dissolution characteristics, and the electrode potential. A method of measuring trace quantities of metallic dissolution and metallic deposition can be assumed to be an effective means of more clearly understanding this corrosion mechanism.

Conventional methods of evaluating migration have been confined to evaluating whether migration occurs. The evaluation is based on observing electrical characteristics such as changes in insulation resistance, which correspond to the precipitation distance attained by the deposits. However, this type of evaluation cannot provide quantitative measurements of changes in electrode weight, which is strongly affected by migration.

The authors of this report used the QCM (Quartz Crystal Microbalance) method to detect minute amounts of dissolution and deposition of electrode materials, and have developed new experimental equipment to measure the process of migration in real time.1,2)

This research has focused on the QCM method to study the growth process of migration in various types of lead-free solder plating (Sn–3.5 mass%Ag, Sn–5 mass%Bi, Sn–9 mass%Zn, and Sn–0.8 mass%Cu). Moreover, to evaluate actual usage conditions, we conducted experiments studying the effects of the reflow processing and flux residue of soldering processes. In addition, we also investigated the anode dissolution characteristics of the elements in each type of solder alloy by measuring the current-potential curve in solution.

2. Experimental

2.1 QCM method1–3)

QCM utilizes the piezoelectric effect of a quartz crystal. This method is able to analyze trace amounts of mass by measuring minute changes in the resonance frequency occurring at the surface of the quartz crystal and correlating these frequency changes with changes in weight. This measurement method has a basic resonance frequency of 5 MHz when using the quartz crystal, and so an increase of 100 Hz of resonance frequency corresponds to a loss of approximately 2.42 μg in mass. As a result, this method is able to detect trace weight changes caused by the occurrence of migration.

Table 1 shows the composition of the electrode materials, the solders composition, flux composition and reflow processing conditions used in these experiments. The electrodes used were plated with each type of lead-free solder using an AT cut quartz crystal with a resonance frequency of 5 MHz (MAXTEK Corp., Ti/Au 5 MHz Crystal). Tin rods with a diameter of 3.0 mm were used to plate the counter electrodes with lead-free solder of the same composition as used on the QCM electrodes. The distance between electrodes was set by using a micrometer to separate the electrodes 0.3 mm from the point at which the QCM electrode was in contact with the counter electrode. One cube centimeter of de-ionized water was dropped onto the electrode interval, and a potentiostat (Hokuto Denko Corp. HA-503G) was used to apply 1.5 volts/DC. At this time, changes were measured in the time variability of both the current and the QCM electrode resonance frequency, with either the cathode or the anode serving as the QCM electrode.

Specimens used to investigate the effects of reflow processing were solder-plated and then heat-treated using reflow
processing conditions. Specimens used to investigate the effects of flux residue were solder-plated and then the QCM electrodes and the counter electrodes were coated with RMA (mildly activated rosin) flux, and finally heat-treated using reflow processing conditions.

After measurements were completed, the electrodes were analyzed after the occurrence of migration (after 1000 s) with a SEM (Scanning Electron Microscope, Hitachi S-4500) and an EPMA (Electron Probe Micro Analyzers, Shimadzu EPMA-8705).

### 2.2 Anode dissolution measurements

The specimens for the experiment were made by cutting each type of lead-free solders, Sn (99.9% pure), and Zn (99.9% pure) into 1.0 cm², and polishing the surface with water-resistant sandpaper. Next, masking was applied to the 0.6 cm round diameter (electrode surface area, 0.28 cm²). Anode dissolution was measured using platinum coated net on the counter electrodes and SCE (Saturated Calomel Electrode) as reference electrodes. After the dissolved oxygen was removed, 0.1 kmol m⁻³ KNO₃ solution was used as the electrolytic solution.

The measuring equipment used consisted of a function generator (Hokuto Denko Corp., HB-105) and a potentiostat. Measurement conditions included a scanning speed of potential at 10 mV/sec, and polarization up to −2000 mV vs. SCE from the natural potential in the direction of the base metal, and a temperature of +25°C. Next, a sweep was made to +2000 mV vs. SCE in the direction of the noble metal, and the current-potential curve was measured.

### 3. Results and Discussion

#### 3.1 Experiment results using QCM method

Figure 1 shows the changes in current and in resonant frequency during the migration generation process of the lead-free solder plating, reflow processing and flux processing. Sharp rises in current indicate short circuiting between...
the electrodes caused by growth of migration. Increases in
resonance frequency indicate metal dissolution at the surface
of the electrodes. Decreases in resonance frequency indicate
metallic deposits or metallic oxide deposits on the surface
of the electrodes.

Changes in current indicated that short-circuiting caused by
migration growth occurred in the following order for the types
of solder plating used: Sn–37 mass%Pb, Sn–5 mass%Bi,
Sn–0.8 mass%Cu, Sn–3.5 mass%Ag, Sn–9 mass%Zn. The
last solder plating, Sn–9 mass%Zn, exhibited no short-
circuiting within the measurement time.

Sn–3.5 mass%Ag, Sn–9 mass%Zn, and Sn–37 mass%Pb
showed a tendency to short-circuit more quickly with reflow
processing than with solder plating. With flux processing,
Sn–9 mass%Zn exhibited short-circuiting more quickly than
with solder plating, while Sn–5 mass%Bi, Sn–0.8 mass%Cu,
and Sn–3.5 mass%Ag did not exhibit short-circuiting within
the measurement time period. Overall, Sn–37 mass%Pb ex-
hibited migration in the shortest amount of time, while lead-
free solder types showed a tendency to take longer. Migration
time for Sn–9 mass%Zn was markedly influenced by reflow
processing and flux.

Changes in resonance frequency indicated that Sn–
37 mass%Pb and Sn–3.5 mass%Ag exhibited greater anode
dissolution quantity with reflow processing than with solder
plating. Flux processing reduced dissolution quantities for all
types of plating. At the cathode, reflow processed specimens
were not confirmed to exhibit major changes in deposition
compared to solder plating.

With Sn–9 mass%Zn, Sn–0.8 mass%Cu, and Sn–3.5
mass%Ag, flux processing did not cause increased deposition
from migration, but instead created a tendency for increased
dissolution. In particular, Sn–9 mass%Zn was confirmed to
have a marked tendency for increased cathode dissolution.

3.2 Effect of reflow processing and flux residue

We considered possible reasons for the quicker short-
circuiting exhibited by Sn–3.5 mass%Ag, Sn–9 mass%Zn,
and Sn–37 mass%Pb after reflow processing.

Figure 2 shows the results of elemental analysis
using EPMA before and after reflow processing for
Sn–3.5 mass%Ag, Sn–9 mass%Zn, and Sn–37 mass%Pb. Be-
fore reflow processing, trace amounts of the elements Ag, Zn,
and Pb were confirmed to be dispersed within the Sn layer.
After reflow processing, re-fusion of the solder elements re-
sulted in Sn layer and Ag3Sn layer in the Sn–3.5 mass%Ag,
and segregation of the Sn, Zn, and Pb was confirmed in
Sn–9 mass%Zn and Sn–37 mass%Pb.

Figure 3 shows SEM photographs, and Fig. 4 shows a
quantitative analysis of cathode surfaces after the experiment.
The major component of migration deposition for Sn–37Pb
was Pb, while the major deposition component for lead-free
solder was Sn.

Figure 5 shows the current-potential curves for Sn–
3.5 mass%Ag, Sn–9 mass%Zn (Solder plating and reflow
processing), Sn, and Zn. Rises in current density indicate dis-
solution characteristics of the anode.

Comparing anode dissolution potentials for Sn and
Sn–3.5 mass%Ag revealed an identical anode dissolution po-
tential of approximately −180 mV vs. SCE (Figs. 5(a), (b).
This phenomenon seems to indicate that the element Sn takes priority in Sn–3.5 mass%Ag dissolution.

The amount of anode dissolution for Sn–3.5 mass%Ag was greatly increased by reflow processing. This increase resulted from the formation of the stable compound Ag₃Sn due to re-fusion, promoting a greater tendency for selective dissolution of Sn than before reflow processing. As a result, the dissolution characteristics of Sn are believed to affect the occurrence of migration.

Next, a comparison of Zn and Sn–9 mass%Zn revealed a notable difference, with the Zn anode dissolution potential at approximately −700 mV vs. SCE compared to an anode dissolution potential for Sn–9 mass%Zn of approximately −180 mV vs. SCE (Figs. 5(c), (d)). Therefore, it is believed that the Zn in the Sn formed an alloy, which gave the condition of a noble metal to the dissolution potential, resulting in the Sn suppressing the dissolution reaction of the Zn. Similarly, large increases in the amount of anode dissolution for Sn–3.5 mass%Ag caused by reflow processing are believed to have resulted from each element separating out, thus lowering the suppression effect and promoting the dissolution reaction. As a result, the dissolution characteristics of these elements affected the occurrence of migration.

The reduced short-circuiting time for Sn–37 mass%Pb resulted from the formability passive film of Pb being smaller than that of Sn, yielding a greater tendency for the dissolution reaction to occur due to Pb segregation caused by re-fusion of reflow possessing. The Pb segregation leading to dissolution is believed to have promoted the occurrence of Pb migration.

Moving next to flux processing, Sn–3.5 mass%Ag, Sn–0.8 mass%Cu, and Sn–5 mass%Bi did not exhibit short-circuiting within the measurement period. This migration resistance is believed to have resulted from the forming Sn ion complex insoluble in water. These Sn ion complex are thought to have obstructed contact between the solder surface and the de-ionized water, suppressing dissolution. On the

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**Fig. 4** Quantitative analysis of cathode surfaces after the experiment.

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**Fig. 5** Current-Potential curves for various metals and solders in 0.1 kmol m⁻³ KNO₃ aqueous solution.

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**Fig. 6** SEM photographs showing the Sn–9 mass%Zn electrode surfaces after the experiment.
other hand, Sn–9 mass%Zn short-circuited in a shorter time period. In the flux processing, Zn (less noble metal against Sn) had preferential reactions with the flux components such as the halogen and organic acids, forming organometallic compounds. As a result, these compounds are believed to have weakened the adhesion between the flux and the electrodes (Fig. 6). Therefore, changes in resonance frequency indicated that Sn–9 mass%Zn exhibited greater cathode dissolution quantity with flux processing than with solder plating or reflow processing. The loss of flux adhesion is thought to have promoted water penetration into the flux pores, speeding the occurrence of migration.

4. Conclusion

We have used the QCM method to evaluate the migration characteristics of lead-free solder plating, investigating the effects of reflow processing and flux residue. Our main conclusions are as follows.

1) When using Sn–3.5 mass%Ag solder plating, reflow processing segregates the stable compound Ag₃Sn layer and Sn layer. The Sn layer selectively promotes the anode dissolution reaction, increasing the occurrence of migration.

2) When using Sn–9 mass%Zn solder plating, the Sn effectively prevents the excessive dissolution reaction of Zn.

However, since reflow processing causes each element to separate out, reflow processing lessens the effectiveness of Sn, thus promoting the occurrence of migration.

3) Flux processing of lead-free solder suppresses anode dissolution and effectively prevents the occurrence of migration. However, with Sn–9 mass%Zn, the lowered adhesion between the flux film and the electrodes is a factor in speeding the growth of migration.

4) Overall, lead-free solder resists migration much better than conventional lead solder. However, in only one of the types of lead-free solder, the base metal Zn formed an alloy with Sn, and the behavior of the Sn–Zn solder showed a tendency to be strongly affected by the actual conditions used.

REFERENCES