Relationship between the Reduction Behavior of Copper and Tin Oxide Films by Formic acid and Solder Wettability

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Void-less solder mounting ensures optimal electrical and heat conduction of soldered components. This requires removal of the oxide films on the metal surfaces. The purpose of this study is to clarify the relationship between the oxide films of the soldering components and solder wettability. The oxide film thicknesses of the copper plate and solder foil were analyzed by transmission electron microscopy, electron energy loss spectroscopy, and X-ray photoelectron spectroscopy. The oxide film thicknesses were approximately 4.0 and 5.3 nm, respectively. CuO and SnOx were both reduced by formic acid and the changes in film thicknesses were measured in real-time. The reduction rate of SnOx was lower than that of CuO. Furthermore, the solder foil and solder ball were melted on a copper plate whose thickness was adjusted to an arbitrary oxide film thickness. Although the contact angles of the solder balls decreased by reducing the thickness of the oxide film, it was necessary to completely remove the oxide film to obtain good solder wettability.

Keywords: Formic Acid, Ellipsometry, in-situ, Solder Wettability, Oxide Film Reduction

1. Introduction

In recent years, with increasing environmental awareness, the demand for electric vehicles (EV) and hybrid vehicles (HV) with high fuel efficiency is growing in the automobile market. In-vehicle power devices used in motor drive inverters of HV and EV are required to have high reliability in severe environmental conditions such as high temperature and vibration. Void-less solder mounting is required to prevent the deterioration of electrical and heat transfer performances caused by the presence of voids. In addition, lead-free solder, which is being substituted to reduce lead contamination, requires removal of the oxide films during the soldering process, such as hydrogen gas. However, the reduction by hydrogen requires a high temperature of approximately 300 °C, making its application to lead-free solder with a low melting point difficult. Additionally, the use of hydrogen is highly dangerous because of its explosive properties.

Researchers have investigated the removal of oxide films using formic acid, in which case the reduction can be performed at a lower temperature. Furthermore, the reaction mechanism using formic acid has attracted significant attention in the field of fuel cells, where the electrochemical oxidation of formic acid in the presence of metals with high catalytic activities such as Pd and Pt has been described. There are few examples in the literature that measure the reduction process of an oxide film by formic acid using time intervals of several seconds. In addition, the exact reduction mechanism for formic acid is unclear. The authors have previously analyzed the oxide film thicknesses of copper, which has been widely used in solder mounting parts, with formic acid in real-time, and clarified the temperature dependence of the reduction rate and activation energy.

In this study, the surface oxide film of lead-free solder was analyzed. Furthermore, the reduction process was measured in real-time when formic acid was used as the reducing agent, and the relationship between the oxide film thickness and the wettability of the solder foil and contact angle of the solder ball was examined.

2. Experimental Method

2.1 Materials

Copper plates (purity: >99.96%, size: 20 × 20 × 2 mm) and solder foils (SnAg3. 0 Cu 0.5, size: 10 × 12 × 0.07 mm) were used for analyzing the oxide film and measuring the oxide film thickness. Solder foils (SnAg3. 0 Cu 0.5, size: 5 × 5 × 0.07 mm) and solder balls (SnAg3. 0 Cu 0.5, size: 1.5 mm) were used for the evaluation of wettability. The rust preventative agent and working oil used during the processing of copper plates were completely removed by immersion and degreasing by ultrasonic waves (using 1-bromopropane). Both copper plates and solder foils were stored in air for six months or more after processing, and native oxide films were initially formed. Formic acid (KANTO CHEMICAL CO., INC.; special grade, purity: >98%) was used as the reducing agent, and N2 gas (99.99% purity) was supplied using an N2 cylinder. CuO (purity 99.9%) and Cu2O (purity 99%) manufactured by Kojundo Chemical Laboratory Co., Ltd. were prepared as reference samples for electron energy loss spectroscopy (EELS). SnO (purity 99.5%) and SnO2 (purity 99.99%) were used as reference samples for X-ray photoelectron spectroscopy (XPS).
2.2 Measurement of Oxide Film by Ellipsometry

In this study, the oxide film thicknesses of copper plate and solder foil were measured by ellipsometry. Ellipsometry is a technique for measuring physical quantities such as film thickness and optical constant of a surface thin film by observing the changes in the polarization state due to sample interaction when the incident light of a known polarization state is reflected on the sample surface. The measurement time is a few seconds, and by continuous measurements, it is possible to analyze the change in the physical quantity of the surface thin film in real-time.

In this study, the change in the thickness of the oxide film in real-time was measured using a high-speed spectroscopic ellipsometer (M-2000, J. A. Woollam Co.,). The wavelength range of the light was 400-1000 nm, the incident angle $\theta$ was 70°, and the data acquisition interval in real-time measurement was set to 0.7-1 s, at which the change in oxide film thickness could be sufficiently confirmed. As shown in Fig. 1, the optical set-up of the ellipsometer has a layered structure of [metal (Cu or Sn)/metal oxide film (Cu$_2$O or SnO)/air].

2.3 Experimental equipment

The experimental set-up is shown in Fig. 2. A uniquely fabricated vacuum chamber (internal volume of 170 mL) was installed between the ellipsometer light source and detector, and the incident and reflected light passed through a quartz glass window in the chamber. The quartz glass window was installed at an angle of 70° so incident and reflected light passed perpendicular to the window surface and no refraction occurred on either side of the window. Therefore, the quartz glass window did not affect the film thickness data.

A copper plate or solder foil was placed on the stage with a built-in heater. A port for supplying formic acid gas, N$_2$, gas, and dry air, and a gas exhaust port were included in the chamber; the latter was connected to a vacuum pump. The internal pressure was monitored by a vacuum gauge installed in the chamber. Formic acid gas was supplied by bubbling liquid formic acid in the pressure tank with N$_2$ gas. This configuration allowed the measurement of the oxide film thickness in real-time by the control of the gaseous atmosphere and pressure in the chamber as well as temperature of the copper plate or solder foil.

2.4 Analysis of surface oxide film of copper substrate and solder foil

Transmission electron microscopy (TEM; field emission-type transmission electron microscope, JEM-2010F, JEOL Ltd.,) and TEM-EELS analyses (beam diameter: $\sim$ 1.0 nm; 863 GIF Tri-diem, Gatan Inc.,) were performed for the native oxide films of the copper plate and solder foil. To prepare a sample for TEM, a carbon film was deposited before and after the focused-ion beam (FIB) processing to protect the outermost surface of the specimen. Then, using FIB processing, a small section of the sample was extracted and thinned to allow the transmission of electron beams. The solder foil was also analyzed by XPS (PHI Quantera II, Physical Electronics, Inc.,). Monochromatic Al Kα (1486.6 eV) radiation was used as the X-ray source. The fermi edge of the solder foil was energy-corrected with reference to the fermi level. For SnO and SnO$_2$, the energy was corrected using the carbon peak (C1s: 285 eV) of the solder foil.

2.5 Measurement procedure of reduction rate of oxide film by formic acid

The procedure for measuring the reduction rate of the oxide film on the copper plate and solder foil is described below.

i. The copper plate or solder foil with a native surface oxide film was placed on the heating stage. The chamber atmosphere was replaced by N$_2$ and thereafter, the copper plate or solder foil was heated to 200 °C.

ii. After the temperature was stabilized, the pressure inside the chamber was reduced. Formic acid gas vaporized by N$_2$ bubbling was introduced at atmospheric pressure while measuring the oxide film thickness in real-time. Formic acid gas was introduced for a time duration of up to 0.5 s.

iii. After the chamber pressure reached the atmospheric pressure, the supply of the formic acid gas was stopped and maintained at that pressure until the oxide film was removed. The real-time measurement of the oxide film was continued during this period.

iv. After the oxide film was removed, the formic acid gas was exhausted, and the copper plate or solder foil was cooled to room temperature and retrieved from the chamber.

![Fig. 1 Optical layout of the Ellipsometer](image)

![Fig. 2 Schematic view of the experimental equipment](image)
2.6 Evaluation of the Relationship between the Copper Oxide Film and Solder Wettability

To determine the relationship between the oxide film thickness of the copper plate and solder wettability, samples with different oxide film thicknesses were prepared by adjusting the time of reduction with formic acid, and the wettability was evaluated by melting the solder on the copper plate. A schematic for the experimental profile is shown in Fig. 3, and the experimental procedure is described below.

i. The copper plate was placed on the heating stage inside the vacuum chamber, and the solder foil and solder ball were mounted at locations other than the measuring part of the ellipsometer on the plate.

ii. The copper plate was heated to 200 ℃ after replacing the chamber atmosphere with N₂.

iii. After N₂ was exhausted, the formic acid gas vaporized by N₂ bubbling was introduced into the chamber; the oxide film was reduced to a predetermined thickness, and formic acid gas was exhausted.

iv. After exhausting the formic acid gas, N₂ was again introduced, and the temperature of the plate was increased to 240 ℃ to melt the solder, followed by cooling and retrieval of the copper plate.

v. The solder foil and solder ball on the copper plate were observed with an optical microscope. Contact angle measurements were performed for the solder balls. The wettability of the solder foil was evaluated with the \( \frac{S_2}{S_1} \) value obtained by dividing the solder spread area \( S_2 \) after melting by the solder foil area \( S_1 \) before melting.

In addition to the sample with complete removal of the copper oxide film, the sample in which the reduction was stopped during the process with partially remaining oxide film, and the sample without the removal of the copper oxide film were also prepared, and the relationship between the copper oxide film thickness and solder wettability was examined.

3. Result & Discussion

3.1 Analysis of surface oxide film of copper substrate and solder foil

From the TEM and TEM-EELS analysis in previous studies, Cu₂O was formed on the surface of the copper plate, and its thickness was approximately 4 nm \(^{14}\).

Fig. 4 shows a TEM image \((\times 4M)\) of the cross-section of the outermost surface of the solder foil. A region of 5.3-nm in length with a different contrast is observed on the surface, which is assumed to be an oxide film. Fig. 5 shows the TEM-EELS data for points 1-5 of Fig. 4. For points 1-4, a characteristic peak is observed at approximately 540 eV, which corresponds to tin oxide film \(^{15}\).

In addition, XPS analysis was performed to determine the valency of the oxide film. Fig. 6 shows the valence band spectra obtained by XPS analysis of the solder foil, and the SnO and SnO₂ standard samples. The peak shape of the solder foil is similar to that of SnO, but the steep change in intensity at 3-4 eV in SnO₂ is only slightly present in the solder foil spectrum. From this, it can be deduced that the solder foil oxide film composition...
is mainly SnO, but also contains some SnO$_2$.

3.2 Measurement of reduction rate of copper oxide film and tin oxide film by formic acid

Fig. 7 shows the data for the real-time measurement of the thicknesses of copper oxide and tin oxide films with an ellipsometer upon the introduction of formic acid gas. Formic acid gas is introduced after 5 s from the start of measurement, and the thicknesses of both oxide films decrease as the reduction progresses after the introduction of formic acid gas. However, the reduction rates are different for both oxide films. The reduction of the tin oxide film is almost completed in 10-15 s, and the average reduction rate is 1.5 nm/s, whereas the reduction of the copper oxide film is completed in approximately 20-25 s, and the average reduction rate is 0.3 nm/s, which is slower than that of the tin oxide film. From these results, it can be predicted that when the solder is mounted on a copper plate and formic acid is introduced, the tin oxide film, which is a solder oxide film, is removed before the copper oxide film.

Based on these results, we acquired data on the relationship between the copper oxide film thickness, wettability of the solder foil, and the contact angle of the solder ball. These are described in the next section.

3.3 Relationship between copper oxide film thickness and solder wettability

Fig. 8 shows the results obtained with an ellipsometer using the procedure described in section 2.6. As shown in Fig. 8(a), the copper oxide film is completely removed by exposing the copper plate to formic acid gas for approximately 45 s. Thereafter, the plate temperature is increased above the melting point to melt the solder foil and solder ball. The plate is exposed to formic acid gas for approximately 10 s (Fig. 8(b)), and the formic acid gas is released when the oxide film is reduced to 0.6 nm, after which the solder foil and solder ball are melted. At approximately 20-30 s, the oxide film thickness increases after being slightly decreased.

This change in film thickness is not considered to reflect relevant behavior. During this time, the formic acid atmosphere is completely evacuated from the chamber, which is then refilled with N$_2$. This causes a rapid pressure drop and subsequent increase which could affect the heating-stage alignment or stress the quartz window, resulting in a change in film thickness.

An identical experiment was conducted on the copper plate in which the exposure time of the formic acid was adjusted between 7 s and 9 s, and the oxide film was reduced to 1.4 nm and 0.9 nm, respectively. As shown in Fig. 8(c), the solder is melted in a state with a native oxide film, i.e. without the removal of the oxide film.

Fig. 9(a) shows the relationship between the copper oxide film thickness during solder melting and the contact angle of the solder ball. The contact angle of the solder ball starts to decrease at approximately 1-nm oxide thickness, and the contact angle decreases to approximately 40° when the oxide film is completely removed.

Fig. 9(b) shows the wettability of the solder foil when the...
copper oxide film thicknesses are 0 and 0.6 nm. The wettability of the solder foil is 100%, when the oxide film is completely removed. However, even when the oxide film thickness is only 0.6 nm, the wettability of the solder foil decreases to 18.1%. However, in the region where the wettability of the solder foil is evaluated, the formic acid gas enters the gap between the solder foil and copper plate, and the reduction occurs, but the surface of the copper plate measured by an ellipsometer is directly exposed to the formic acid gas. For this reason, the thickness of the copper oxide film in the region where wetting is evaluated is less likely to be reduced than at the ellipsometer measurement point, and the film thickness is likely to be greater than 0.6 nm. For a reduction time of 45 s, which is sufficient, the oxide film is completely removed even in the gap between the solder foil and copper substrate, and good wetting is obtained.

4. Conclusion

To establish the relationship between the reduction of copper and tin oxide films by formic acid and solder wettability, the following results were obtained by the surface analysis of the oxide films and real-time measurements using an ellipsometer.

- TEM, TEM-EELS, and XPS analyses of the copper plate and solder foil confirmed that the respective oxide films mainly comprised CuO and SnO, and the film thicknesses were approximately 4 nm and 5.3 nm, respectively.
- Based on the real-time measurements of the oxide film thicknesses with an ellipsometer, copper oxide and tin oxide films were both reduced by formic acid, with the reduction rate of the tin oxide film higher than that of the copper oxide film.
- Although the contact angles of the solder balls were reduced by decreasing the thickness of the copper oxide film via formic acid reduction, it was necessary to completely remove the oxide film of the solder foil to obtain good solder wettability. However, it is important to note that the thickness of the copper oxide film in the area between the solder foil and the copper plate was not evaluated in this study. Since formic acid enters the gap between the solder foil and the copper plate, and reduction occurs there, it is possible that the reduction rate in the gap is different compared to the copper plate surface on which the solder foil is not mounted. In order to clarify the relationship between the wettability of the solder foil and the copper oxide film more accurately, the measurement of the thickness of the copper oxide film under the solder foil should be investigated further.

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