Low-resistance copper conductive balls that prevented migration

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ABSTRACT
The demand for flexible displays (e.g., foldable and rollable displays) has recently increased, thus necessitating the development of various component technologies. An anisotropic conductive film, which is a conventional surface mount technology, is deemed more necessary than soldering for the implementation of a flexible display. However, it is still difficult to secure the electrical conductivity and reliability of the conductive ball used in the anisotropic conductive film. In this paper, a copper conductive ball having a lower resistance than the conventional conductive ball was fabricated. It has a lower contact resistance than nickel and gold, and the reliability issue, which is a disadvantage of copper, is secured by blocking the reaction with oxygen and coating a thin corrosive solution.

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1. Introduction

Although ultra-high-definition (UHD) technology has been developed to facilitate the manufacture of 4K resolution displays, the rapidly growing virtual reality display industry requires a much higher resolution. Furthermore, flat-panel displays, such as those used in TVs, smartphones, tablets, and advertisement panels, are being replaced with flexible displays regardless of the location and display size [1–6]. In order to achieve such high-resolution display changes, fine-pitch electronic packaging technology is required. Although soldering is used for connecting conductors in existing displays, it has the disadvantage of increasing the area of the substrate, and it cannot be used for flexible substrates. To overcome this problem, manufacturers of modern electronic products are using anisotropic conductive film (ACF) instead of ball grid array packaging technology. In ACF, a metal-coated spherical polymer called conductive ball is dispersed in an adhesive [7–10]. The conductive ball is designed to be mechanically connected and to transmit electricity in a vertical direction. It can also be used to effortlessly connect high-density and high-performance devices. However, capturing the conductive balls in the ACF becomes increasingly difficult as the width of the fine-pitch bumps decreases. This leads to higher contact resistance or agglomeration, which may result in a short circuit [11, 12]. Currently, nickel and gold are mainly used as metal coatings for conductive balls. When comparing nickel and gold, the former is more commonly used because it is inexpensive, whereas the unit price of gold is extremely high, and its contact resistance is also high. However, nickel-coated conductive balls also pose a problem in that they cannot supply a smooth current between devices. Accordingly, researchers are working toward identifying metallic coating materials that can help overcome these drawbacks. In this study, we developed a copper-coated conductive ball that can lower the contact resistance at fine pitch, and it is cheaper than gold [13, 14]. The electrical conductivity of copper (59.6 MS/m) is higher than that of gold (45.2 MS/m) by about 30%. The surface of the copper coating was uniform, and the desired coating thickness was obtained by using a controllable electroless plating method. An additional corrosive coating was provided in order to prevent migration that occurs when copper is exposed to moisture. In the case of copper, migration resulting from the metal’s contact with oxygen can result in a short circuit, thereby adversely affecting the connection between conductive balls and bumps, which would result in high contact resistance. An extreme environment was created for copper sheets and copper conductive balls in order to confirm the effectiveness of the corrosive coating in preventing copper from reacting with oxygen. The copper-coated conductive ball has the potential to provide electrical properties suitable for the fine pitch of next-generation displays and various electronic products.

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2. Experimental

2.1. Preliminary experiments

Spherical polymer beads with a diameter of 3 μm were fabricated and treated with reagents (Meltex, Japan) of cleaners, activators, and accelerators for enhancing their surface activity. We performed electroless plating with nickel and copper plating solutions to provide a metal coating on the surfaces of the beads. A flexible printed circuit board (FPCB) with a fine pitch of 20 μm was used for measuring contact resistance.

2.2. Measurements

A scanning electron microscope (SEM) was used to determine the surface uniformity and shape of the fabricated conductive balls, and energy dispersive spectrometry (EDS) was used to confirm the metal coating on the surface. Copper-coated conductive balls were used to prepare the ACF. The dimensions of the FPCB were 48 mm × 33 mm, and its electrode’s dimensions were 2 μm × 2 μm. The thickness and pitch of the FPCB were 10 and 20 μm, respectively. A sample was prepared through the thermocompression bonding of the ACF between the FPCB and indium tin oxide glass, and the contact resistance was measured by using a four-point probe. Finally, to measure reliability data, we maintained an internal environment at a temperature of 85°C and a humidity of 85% by using reliability equipment.

2.3. Polymer bead surface modification and washing

Surface modification of the metal beads was performed by applying a metal coating to their surface. The beads were cleaned and washed in order to remove foreign substances from the surfaces. The surfaces were treated with a surface modification solution, referred to as an activator, which could react with the metal ions on surfaces, and the beads were then washed with water. Finally, after coating an accelerator, which acted as a catalyst and increased the reactivity of the surface coating, the polymer beads were again washed with water.

2.4. Conducting copper coating and corrosive coating on the surface of polymer beads to produce conductive balls

A nickel plating solution was prepared for coating nickel on the surface-modified polymer beads by using the dropping method. This method involves placing the polymer beads in a reducing agent solution, stirring, and adding a nickel ion solution at a constant rate in order to induce a reaction. Since the pH of the reducing agent solution changes as more nickel ion solution is added, a pH meter was used to maintain an adequate pH during the nickel coating. In view of the possibility of overloading, which could occur due to an excessive addition of the nickel solution given the specific surface area of the polymer bead, the specific surface area of the polymer beads was obtained by using Equation (1)

\[
\text{Specific surface area} = \left( \frac{m^2}{g} \right) = \frac{1}{4} \frac{\text{sphere area}}{\text{sphere mass}} = \frac{4\pi r^2}{\rho \frac{4}{3} \pi r^3} = \frac{3}{r \rho}
\]

where \( r \) is the radius of the sphere and \( \rho \) is the specific gravity. The calculated specific surface area could be used to calculate the amount of nickel coating solution to be added. The amount of nickel was then used to fabricate nickel conductive balls. After washing the nickel conductive balls, we prepared a copper solution based on the specific surface area obtained from Equation (1), placed it over the nickel conductive balls, and stirred the solution for about 30 min. In order to reduce the oxidation of copper, the plating solution was poured into a beaker, the pH and temperature were adjusted, and the dissolved oxygen was removed by passing nitrogen gas through the beaker for 30 min. Ultrapure water with very low dissolved oxygen content was used as deionized (DI) water for adjusting the concentration of the plating solution. After stirring, we obtained copper conductive balls, which were washed with water and freeze-dried in a flask. An oven was used to remove moisture, resulting in rapidly hardened conductive balls. Moisture between the balls caused them to stick together, whereas freeze-drying caused them to separate. The freeze-drying method involved sublimation, in which the moisture in the flask changed from ice to gas at the low temperature and low pressure maintained in the flask. Perfect copper conductive balls were obtained after freeze-drying for three days. Figure 1 shows an image of a conductive ball’s surface, which was examined by EDS to determine whether the coating was appropriate.

Figure 1(a) shows an image of the surface of a copper conductive ball, and Figure 1(b) shows an image where the copper ions are mapped to the surface in Figure 1(a). It is evident that the mapping is almost similar to the spherical shape of the conductive ball; therefore, copper is coated on the surface. In order to ensure these conditions, we observed the peak value of each ion in the graph of Figure 1(c). Maximum values of 93.25 and 1.69 wt% were observed for copper and nickel, respectively. Finally, a corrosive coating was applied in order to prevent the migration of the copper conductive balls.
The balls were first washed with water and then ultrasonically cleaned to remove foreign substances on their surface. The corrosive coating solution and DI water were combined in an appropriate ratio, and the resulting solution was stirred for about 30 min. Ultrapure water with a dissolved oxygen content of 0.46 ppb was used as DI water in order to reduce copper oxidation during coating. The prepared conductive balls were placed in the mixed solution through a stirrer, and the solution was stirred at a speed of 250 rpm for up to 3 min in order to coat the conductive balls.

3. Result and discussion

3.1. Corrosive coating copper conductive ball reliability change (temperature 85°C, humidity 85%)

Prior to proceeding with the experiment, corrosive coating was performed on a copper sheet to observe changes. The copper sheet had dimensions of 50 mm × 50 mm, and the changes were found to be dependent on the concentration of the corrosive coating and coating duration. Figure 2 shows a photograph of changes that occurred on the copper sheet at different coating times.

Figure 2(a) shows a reference copper sheet without rust. Figure 2(b) to (e) show photographs of the surface of the sheet after it was placed in the reliable equipment at a temperature of 85°C and humidity of 85% for 24 h to observe the changes caused by an extreme environment. Figure 2(b) shows that copper was oxidized in the presence of oxygen. However, Figure 2(c) to (e) show that there were no major problems despite the presence of slight oxidation. Figure 3 shows a graph of the oxidation area of the copper sheet depicted in Figure 2. The overall copper sheet image was converted into 8-bit, and the oxidized part was confirmed and quantified based on the contrast.

Figure 3 shows that in the case of the uncoated copper sheet, an area close to about 30% of the total area was oxidized after 24 h. However, all copper sheets coated with an oxide film were confirmed to have an oxidation area of less than 3%. It was also found that when the oxide film was coated for more than 30 s, more than 95% of the
Figure 3. Oxidized area of corrosive coating time.

copper sheet and oxygen were blocked. Figure 4 confirms that the change is proportional to the concentration of the corrosive coating.

Figure 4 confirms the changes based on the concentration of the corrosive coating. Figure 4(a) and (b) are identical to the images shown in Figure 2. Figure 4(c) to (e) confirm the changes based on the concentration of the corrosive coating. When compared with the image in Figure 4(b), the coated copper sheet showed very little oxidation. Figure 5 shows a graphical representation of the oxidation area according to the concentration of the corrosive coating.

Figure 3 shows that an area close to 30% of the uncoated copper sheet was oxidized, whereas less than about 4% of the area of the coated copper sheet was oxidized. The reason for showing a slightly larger oxidation area compared with Figure 3 is that there was a stain on the surface of the copper sheet before coating. These results confirmed that the corrosive coating prevented oxidation by blocking the copper surface and oxygen. Corrosive coating was applied to copper-plated conductive balls based on the results of the above experiment. Here, the copper plating was 0.5 μm thick. Figure 6 shows the surface of a copper conductive ball without corrosive coating after the reliability test (at 85°C and 85% humidity).

Figure 4 shows that there were no major problems on the surface of the copper conductive ball, and Figure 6(b) shows that migration occurred on the surface. Figure 6(c) shows that the size of the migration increased gradually, and in Figure 6(f), the size increased after a time lapse of 96 h. We also confirmed that the conductive ball had a completely different appearance than that shown in Figure 6(a). These results indicated that the copper conductive balls were susceptible to moisture, and if used in a circuit as is, the copper oxide expands and reduces the electrical conductivity, potentially causing a short circuit. The reaction of copper with moisture to form copper oxide is as follows:

\[
\text{Cu} + 4\text{H}_2\text{O} \rightarrow \text{Cu(OH)}_2 + \text{O}_2 + 3\text{H}_2 \\
\text{Cu(OH)}_2 \rightarrow \text{CuO} + \text{H}_2\text{C}
\]

Figure 7 shows the reliability test results after the application of a corrosive coating to the same copper conductive ball shown in Figure 6 for surface confirmation.

Figure 7(a) to (f) show that the copper coating is not oxidized other than on the surface of the conductive ball. Moreover, there are clear differences when compared with Figure 7(f), which shows a copper conductive ball after 96 h. It was found that the corrosive coating prevented the formation of copper oxide and contact of the copper surface with moisture. Based on these results, a corrosive coating has been found to have a significant

Figure 5. Oxidized area of corrosive coating concentration.
influence on the oxidation of copper conductive balls. In particular, we confirmed that excellent reliability test results were obtained for a conductive ball coated with the corrosive coating.

### 3.2. Corrosive coating thickness optimization

Based on previous experiments, surface oxidation of copper conductive balls could be prevented by applying a corrosive coating. The data sheet of the corrosive coating indicated that the thickness was constant from 0.94 wt% or more to about 13 μm over 2 min. The corrosive coating time and concentration of the copper conductive balls were optimized in order to determine whether this change in the thickness of the corrosive coating is also applicable to copper conductive balls.

First, the change in the thickness with time was confirmed in Figure 8, which shows a cross section using focused ion beam (FIB) SEM to evaluate the variation of the coating thickness of the conductive ball surface with coating time. Platinum was coated on the conductive ball for the other single layer. However, polymer conductive balls treated with an ion beam to cut a cross section could melt. When a thin film layer was used between the platinum and copper plating, the thickness in Figure 8(a) had a minimum value of 5.6 nm and a maximum error

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**Figure 6.** Reliability test (temperature 85°C and humidity 85%) of conductive copper balls without corrosive coating: (a) 0 h, (b) 12 h, (c) 24 h, (d) 48 h, (e) 72 h, and (f) 96 h.

**Figure 7.** Reliability test (temperature 85°C and humidity 85%) of conductive copper ball with corrosive coating: (a) 0 h, (b) 12 h, (c) 24 h, (d) 48 h, (e) 72 h, and (f) 96 h.
Figure 8. Cross-sectional scanning electron microscope (SEM) image of coating thickness according to corrosive coating time: (a) 30 s, (b) 60 s, (c) 120 s, and (d) 180 s.

Figure 9. Corrosive coating thin film thickness according to coating time.

of 14.3 nm. It is evident that a uniform thickness cannot be achieved for a short coating time. Figure 9 shows the thickness with respect to the coating time in Figure 8.

Apparently, the error was 0.8 nm or less for 60–180 s of coating time. It was also confirmed that the thickness of the coating ranged from about 12 to 13 nm, which converged to a maximum of 13 nm. Accordingly, the optimization time that reduced the thickness error the most was set to 120 s, and the change in the thickness with the concentration was investigated. Figure 10 shows a cross-sectional image of a conductive ball used to confirm the thickness by concentration of the corrosive coating solution.

In contrast to the other images, Figure 10(a) shows that the thickness of the coating was very small when the coating concentration was 0.47 wt%. Furthermore, the coating concentration was very low compared with the specific surface area of the conductive ball. The target thickness was achieved at a concentration exceeding 0.94 wt%, as shown in Figure 10(b).

Figure 11 shows a graphical representation of these figures in that the target thickness of 13 nm could be produced at a concentration of 0.94 wt% or higher. Although there is a certain error range, it can be seen that the target thickness is almost nonexistent when the concentration is 1.86 wt%. These experimental results confirmed the time and thickness optimizations, and it was found that the thickness converged to a value similar to that specified in the data sheet. Based on the above results, we performed corrosive coating in order to obtain reliable data after optimizing the thickness of the copper conductive ball.

3.3. Copper conductive ball thickness optimization

We attempted to optimize the thickness of the copper plating before proceeding with the corrosive coating. First, copper plating was performed on a nickel conductive ball, yielding copper plating with four different thicknesses of 0.1, 0.25, 0.5, and 0.75 μm. Figure 12 shows a photograph of a cross-sectional view of a copper conductive ball with different coating thicknesses and a copper conductive ball.

It was evident that the surface of the copper conductive ball was nearly identical. We obtained measurements
for the cross section by using an FIB SEM in order to check the thickness of the copper plating. Figure 12(d) to (f) show that the coating has the target thickness. It is worth noting that the results obtained by calculating the specific surface area for the target thickness of copper plating and the copper-plated conductive ball are consistent. Furthermore, we measured the contact resistance of the copper conductive ball whose thickness was confirmed in the previous experiment, and the difference in contact resistance according to the presence or absence of a corrosive coating is shown in Figure 13.

When the thickness was small (0.1 μm), the resistance was 3.4 mΩ. In addition, the conductive ball with a corrosive coating showed a high resistance of about 3.6 mΩ. This implies that it is lower than the electrical conductivity of copper. This is because the nickel-coated interior was affected more than the copper plating thickness of 0.1 μm. The results supporting these observations are seen from the contact resistances of 0.25 and 0.5 μm with increasing thickness. When the coating was 0.25 μm thick, the contact resistance had a value of 1.1 mΩ, and when the coating was 0.5 μm thick, the contact resistance was 0.9 mΩ. It was also found that the conductive ball with a corrosive coating had a lower resistance than that with a copper plating of 0.1 μm. Based on these results, we identified the most optimal thickness to be 0.5 μm. Figure 14 compares the contact resistances of nickel and gold conductive balls that are commercially available.

![Figure 11](image1.png)  
**Figure 11.** Corrosive coating film thickness according to coating concentration.

![Figure 12](image2.png)  
**Figure 12.** Conductive ball surface and cross-sectional image according to copper plating thickness: (a) 0.1 μm, (b) 0.25 μm, (c) 0.5 μm, (d) 0.1 μm cross section, (e) 0.25 μm cross section, and (f) 0.5 μm cross section.

![Figure 13](image3.png)  
**Figure 13.** Contact resistance by thickness of corrosive coating.
The resistance of the copper-coated conductive ball is lower than that of the gold-coated conductive ball. Copper has a higher electrical conductivity than gold; therefore, it has a lower resistance. Copper conductive balls are deemed appropriate for use because their resistance is about three times lower than nickel conductive balls due to their high unit price. In addition, copper conductive balls have lower contact resistance and lower unit price compared to gold balls. If copper migration, which is a significant problem, can be prevented, we believe that the most efficient conductive balls can be developed. Figure 15 shows a graph of the reliability test for the copper conductive balls.

The test was performed for 144 h in an environment with a temperature of 85°C and a humidity of 85%. Initially, all samples had resistances of less than 1 mΩ. However, after 24 h, the conductive ball without any corrosive coating showed an increased resistance close to 1 mΩ, and the resistance increased to 1.2 mΩ after 144 h. Based on these results, the surface of the conductive ball migrated in a reliable environment and affected the resistance. In contrast, the resistance of copper conductive balls with a corrosive coating increased slightly at first, but remained lower than 1 mΩ even after 144 h. Therefore, it is evident that the corrosive coating prevented migration, and the resistance did not increase significantly. These results show that the corrosive coating suppressed migration, which is a major problem with copper, and maintained the contact resistance of copper at a steady level.

4. Conclusion

In this study, we fabricated conductive balls with a new coating material that can lower the contact resistance of the balls. Copper deposits were formed on the surface of copper when the surface came in contact with moisture, and they prevented the contact resistance or caused a short circuit, which rendered the conductive balls unsuitable for use. Copper (0.94 mΩ) has about 150% higher electrical conductivity than gold (1.5 mΩ), so it was determined that conductive balls with very good performance could be manufactured if only the migration problem was solved. The results of testing to determine whether the corrosive coating prevented copper migration showed that migration could be prevented by forming a thin film on the copper surface to prevent moisture from coming in contact with the copper coating. In addition, the coated conductive ball increased contact resistance by about 1.3% as a result of the reliability test in an extreme environment with 85% humidity at 85°C. However, it was confirmed that the contact resistance of the conductive ball without corrosive coating increased by about 200%. Based on these results, an experiment was conducted by applying a film to a conductive ball coated with copper. The experimental results showed that the copper conductive ball coated with the film (corrosive material) had a lower resistance than gold and that the corrosive coating formed a thin film on the surface of the copper conductive ball that not only prevented the copper surface's reaction with moisture, but also inhibited copper migration. Based on the reliability data, a resistance of 1 mΩ or less was observed after 144 h. In conclusion, it is inferred from the long-term reliability data of copper conductive balls with a corrosive coating that the highly efficient copper conductive balls can be used to replace gold and nickel-coated balls.

Disclosure statement

No potential conflict of interest was reported by the author(s).
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