Migration of Conductive Ink using Silver-Copper Solid Solution Powder

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Summary

We developed the conductive ink using silver (Ag)-copper (Cu) solid solution powder and investigated an ionic migration phenomenon of the conductive ink. The conductive ink is made by dispersing the powder in phenol resin. This powder has a shell structure. The Ag concentration at the surface of the powder is higher than an average Ag concentration in the bulk, and Ag concentration decreases toward inside of the powder. The Ag concentration of about 85 wt% in the Ag-rich phase dose not strongly depend on the average Ag concentration, and the thickness of Ag-rich phase increase with the average Ag concentration. Though this ink includes Ag, in which ionic migration occurs most easily, and Cu, which is oxidized easily, the migration occurrence of this ink including the powder with Ag of 5 wt% was similar to that of Cu conductive ink and Ag migration was not observed.

Keywords: *migration, silver-copper solid solution powder, conductive ink, graded structure*

1. Introduction

A failure occurs occasionally when electronic components are operated for a long time on field use. One of these failure includes an insulating breakdown at low electric field under humid environment, and this type of failure causes a short-circuit eventually. Such a phenomenon first reported in detail by Kohman in 1955 [1]. He found that this insulating failure was accompanied with the movement of the contact metal on or inside the substrate insulator. It was concluded that this metal transports, named "silver migration", occurs by an electrochemical mechanism in which a metal element on high potential conductor is ionized under the existence of water and the ion is moved on the insulator toward low potential conductor, and the metal precipitates on the substrate between conductors.

Further, the generation of conductive anodic filaments (CAF) was found, in which the metal precipitates on the surface of fiber in the epoxide insulator. It was also found that the migration depends strongly on the environmental conditions, such as temperature, humidity and electric field [2-4].

On the other hands, in order to lower a cost of consumer electronic products, a conductive ink is printed with screen mask, and hardened at a low temperature in the air for making wiring. It is widely used that a conductive ink is made by dispersing Ag or Cu powders in a resin. An electric characteristic of Ag conductive ink is satisfactory due to its low specific resistivity. However,

there is a demerit that a migration occurs easily in Ag. Although Cu conductive ink is superior than Ag conductive ink because of lower trend of the migration, it is easily oxidized.

To overcome these problems, in the present work, the conductive ink containing Ag-Cu solid solution (SCSS) was developed [5]. In this powder, Ag concentration at the surface is higher than inside of the powder. The migration characteristics of this conductive ink will be compared with Ag, Cu and Ag-Cu mixed conductive ink, and the migration mechanism of SCSS ink will be discussed.

2. Experimental Methods

2.1 Experimental samples

The sample used in the present experiment are listed in Table 1, where composit and powder state of each sample is shown. After dissolving Ag into Cu, SCSS powder was made by atomizing method in non-active nitrogen gas. The composition ratios of Ag were 5 and 20, 30, 40, 85 wt%, these are named F, G, H, I and J respectively in Table 1. SCSS conductive ink was made by mixing and dispersing these powders in phenol resin (resorcinol type) using automatic mortar. Glycol ether was used as solvent. For a comparison with SCSS ink, we also made conductive ink, consisting of mixed powders of Ag and Cu (MSC). The mixing ratios of Ag in MSC ink were 2.5 and 5, 10, 20 wt% and named B, C, D, E respectively in Table 1. The pure Cu

(named A) and pure Ag (K and L) were also tested. A paper phenolic board was used for an insulation substrate. The gap for electrodes, which were printed directly on the substrate with screen mask, was 0.5mm (30mm in length) and the specimen was hardened in a furnace at 150 °C for 30 minutes in the air by using an electric oven.

2.2 Testing methods

Figure 1 shows a steady test method with a circuit for measuring insulation resistance under a damp heat environment. In order to cause a migration, specimen was left in the condition of steady temperature (40, 65 and 85°C) and steady humidity (95%R.H.) for about 500 hours. The applied voltage between electrodes was DC 100 V. A change of value of an insulation resistance was recorded by a multi-plotter. For observing the migration, optical microscope and scanning electron microscope (SEM) were used after the test. Electron probe micro analysis (EPMA) (Hitachi S-2700 and Horiba EMAX5770), field

Fig.1. Testing method of migration and resistance.

Table 1. Component and powder state of conductive ink.

Sample	Composition(wt%)		Powder state
	Cu	Ag	
A (pure Cu)	100	0	dendritic
B (mixed Ag and Cu)	97.5	2.5	A + K
C (")	95	5	"
D (")	90	10	"
E (")	80	20	"
F (Ag-Cu solid solution)	95	5	spherical
G (")	80	20	"
H (")	70	30	"
I (")	60	40	"
J (")	15	85	"
K (pure Ag)	0	100	spherical
L (")	0	100	petaline

emission transmission electron microscopy (FE-TEM) (Hitachi HF2000) and X-ray photoelectron spectroscopy (XPS) (ULVAC Model5400)) were used to estimate the metal composition, and X-ray diffractometer (XRD) (Rigaku RAD-B) using Cu-K α (1.541 Å) was used to analyze the crystal structure of powders.

3. Results and Discussion

3.1 Structural analysis

Figure 2 shows SEM images of the various printed conductors. As shown in Figs.2 (a) and (b), SCSS conductive powder and Ag powder used for MSC ink have spherical shape with diameter of an approximately less than 10 μ m. A shape of Cu powder (Fig.2(c)) in Cu conductive ink is dendritic. The conductive ink can not be made by Cu powder with spherical shape because of the poor contact between powders. The typical shape of Ag powder used for Ag conductive ink is petaline, as shown in Fig.2 (d).

Fig.2. SEM view of several samples, (a) SCSS Ag-5 wt% of sample F, (b) spherical Ag of sample K, (c) dendritic Cu of sample A, (d) petaline Ag of sample L.

Figure 3 shows the distribution of Ag on a powder surface in a sample F (SCSS, Ag-5 wt%) observed by FE-TEM. It is found that a powder consists of several grains, and Ag piles up in large quantities on grain boundaries. XPS revealed that the Ag concentration on the powder surface in this sample is about 35%, which is much higher than the average Ag concentration of 5%. Metal compositions estimated by the integral intensity of Ag3d and Cu2p lines in XPS specrum, taking into account the relative sensitivity of these lines. These results suggest that Ag is

concentrated at the surface, and the powder has a graded-composition structure in which Ag concentration decreases towards inside.

Fig.3. Ag map for SCSS powder of sample F (Ag-5 wt%) observed by FE-TEM.

Fig.4. X-ray diffraction patterns of the samples.

Figure 4 shows XRD patterns of the samples. The powders are polycrystalline. It is found that the diffraction peaks related to Ag and Cu coexist in one sample, suggesting the presence of two phases of solid solutions in SCSS powders. One of which is a Ag-rich phase in which Cu is dissolved into Ag, and the other is a Cu-rich phase in which Ag is dissolved into Cu. It is interesting to note that the positions of the diffraction peaks related to Ag and Cu do not depend on Ag concentration in MSC samples (A-F), on the other hand, these peaks in SCSS samples (F-J) shift depending on the Ag concentration.

Figure 5 shows the relationship between Ag concentration and lattice constants calculated from Cu(111) and Ag(111) peaks in Fig.4, where the Ag concentration is changed from wt% to

mol%. The lattice constant of Ag-rich phase shows the large deviations from that of Ag with addition of Ag of 3 mol% (5 wt%) in the powder. However, it does not strongly depend on further increase in the average Ag concentration. On the other hand, the lattice constant of Cu-rich phase increases gradually with increase in Ag concentration. However, it also tends to saturate over 20 mol% (30 wt%). If Vegard's law is applied to the results shown in Fig.5, we can estimate Ag and/or Cu concentrations in these phases. For example, in a sample F (Ag-3 mol%) and J (Ag-77 mol%), the Ag concentrations in Ag-rich phase are about 83 and 87 mol% (89 and 92 wt%), respectively, and they are about 3 and 14 mol% (4 and 22 wt%) in Cu-rich phase, respectively. The Ag concentrations in these two phases do not coincide with the average Ag concentrations. The phase with higher Ag concentration should exist on the surface of powders, as expected from the XPS measurements. These results indicate that SCSS powder has a shell structure in which Ag-rich solid solution layer exists at the surface of Cu-rich solid solution core. The thickness of Ag-rich phase increases keeping about the same Ag concentration for the increase in the average Ag concentration in the powder. The situation is also similar to Cu-rich phase except the low Ag concentration region, that is, only the volume of Cu-rich phase with about the same composition decreases with increase in the average Ag concentration.

Fig.5. Relations between lattice constant and Ag concentration.

3.2 Migration characteristics

3.2.1 Observation by optical microscope

Figure 6 shows the observation of migration by optical microscope after keeping specimen for 1000 hours at the condition of 40°C, 95% R.H.. As seen in the figures, migration is observed between conductors after the test irrespective of a kind

of conductive ink. It was found that the type of migration is the so called CAF (Conductive Anodic Filaments), where migration occurs like a filament along a fiber in the base material from an anode, and it is not observed on its surface.

In the specimens of SCSS, the number of CAF and quantity of moved metal increases with increase in Ag concentration, as shown in Figs.6(c), (e), (g) and (i). This trend is also observed in the specimens of MSC, as shown in Figs.6(d) and (f). Though the migration occurs in Cu sample too, as shown in Fig.6(b), CAF due to migration is a little. In the specimens of Ag shown in Figs.6(h) and (j), migration occurs more remarkably than in specimens of SCSS, as suggested by many CAF. The edges of these conductors discolor black, may be due to the oxidation. It is found that the shape difference of Ag powder

dose not affect on the degree of migration, because the occurrence of migration of both Ag conductors shown in Figs.6. (h) (spherical-shaped) and (j) (petaline-shaped) are similar.

3.2.2 Change of insulation-resistance value

Figure 7 shows the changes of insulation-resistance value with time under a wet-proof test in condition of 40°C, 95 % R.H.. In a few minutes after the starting of the test, the resistance value decreases quickly several orders from about 10^{12} to $10^8 \Omega$ by the absorption of moisture, and then it holds on stable state. After certain period of time, the value of resistance goes down rapidly. It is considered that this rapid drop of resistance is due to the formation of the conductive path of precipitated metal caused by migration. The value of resistance goes lower unstably with repeating up and down by the progress of migration with time. Here, we defined a time when the resistance value becomes 1 order lower than that of first value after moisture absorption as a failure time.

Figure 8 shows relationship between failure time and Ag concentration. In the figure, the solid line shows failure times of SCSS and dashed line represents failure times of MSC. Failure times of Ag (L and K) are shortest, and failure time of Cu (A)

Fig.6. Optical view of migration of samples exposed to the moisture of 40°C, 95% R.H. at 200 V/mm for 1000 hours, (a) as prepared, (b) pure Cu of sample A, (c) SCSS Ag-5 wt% of sample F, (d) MSC Ag-5 wt% of sample C, (e) SCSS Ag-20 wt% of sample G, (f) MSC Ag-20 wt% of sample E, (g) SCSS Ag-30 wt% of sample H, (h) spherical Ag of sample K, (i) SCSS Ag-40 wt% of sample I, (j) petaline Ag of sample L. The polarity of an applied voltage is shown in the figure.

Fig.7. Change of resistance with time under a wet-proof test for various conductive ink.

Fig.8 Relationships between Ag concentration and failure times.

is longest as compared with the other specimens. As Ag concentration increases in SCSS specimens, a failure time is shortened. The failure time of MSC decreases rapidly at high Ag concentration. In comparison with samples of the same concentration of Ag, it is clear that the migration occurs easier in MSC than in SCSS.

Figure 9 shows that the temperature dependence of failure time of various conductive ink. A failure time by migration can be formularized by the following experimental expression [6],

$$t_{MTF} = a(H)^b \exp(E_a/k_b T), \quad (1)$$

where t_{MTF} is a mean failure time (h), a, b and d are constants, H is a relative humidity, E_a is an activation energy (eV), k_b is Boltzman constant, T is an absolute temperature (K).

Fig.9. Arrhenius plot of the temperature dependence of failure time of various conductive ink (E_a =activation energy).

An activation energy of sample F (SCSS, Ag-5 wt%, $E_a = 0.23\text{eV}$) is nearly equal to that of specimen A (pure Cu, $E_a = 0.21\text{eV}$). The value of specimen L (pure Ag) is 0.34eV . This result indicates that the changing mechanism of resistance value of SCSS ink including Ag of 5 wt% is similar to that of Cu ink. Namely, it means that Ag in SCSS powder is not practically influential for a cause of the drop of insulation resistance.

3.2.3 Elemental analysis

Figure 10 shows the examples of elemental distribution map observed by EPMA between conductors of sample F (SCSS, AG-5 wt%) after a migration test for 1000 hours. As shown in Fig.10(c), Ag is not detected in EPMA analysis of the place where migration is seen by SEM photograph (Fig.10(a)). Only Cu is detected in the same area as shown in Fig.10(b). Although it is undeniable that Ag exists less than a detection sensitivity, it is considered that almost Ag dose not migrate because of immovable state in solid solution.

Fig. 10. EPMA photographs of sample F after migration test, (a) SEM photograph of migration, (b) Cu-K α map of the same area (a), (C) Ag-L α map of the same area (a). The polarity of an applied voltage is shown in the figure.

3.2.4 Migration mechanism of SCSS ink

Ag migration mechanism of forming CAF may be expressed by the following reaction formulae [1],[7].

As shown by a formula (2), under the electric field, Ag is ionized at the anode, and Ag^+ moves toward cathode in the water on the substrate. Ag^+ precipitates on the substrate between the electrodes as AgOH, Ag_2O or Ag, according to formulae (3) -(6). Ag_2O is also reduced by light or reducing agents. The migration mechanism of Cu is similar to Ag.

Though SCSS ink includes Ag, its migration characteristic, especially in sample F, is similar to Cu. This behavior may be explained as follows:

As referred to the standard H^+ electrode, the electrode potential of Cu^{2+} is 0.340V , Cu^+ is 0.520V , and Ag^+ is 0.799V [8]. Namely, Cu can be ionized easier than Ag. Therefore, if Ag and Cu coexist in atomic scale as in the solid solution, Ag can not be ionized [7].

Thus, while Cu migrates, the Ag migration may be suppressed. The degradation of migration, as shown in Fig.9, characteristic with increase in average Ag concentration may be due to the increase of the Ag pile up on the grain boundaries in the powder.

But, in case of mixed powder of Ag and Cu, this reaction can not occur easily, because Ag and Cu do not contact in atomic

scale. Thus the migration of Ag and Cu occur independently in the mixed powder.

4. Conclusion

In this study, we developed the graded Ag-Cu solid solution (SCSS) powder, and investigated an ionic migration of the conductive ink using by this powder. It was found that this powder has a shell structure in which Ag rich solid solution layer exists on the surface of Cu rich solid solution core.

The occurrence of migration of conductive ink using this SCSS powder including Ag of 5 wt% was nearly equal to Cu.

The present result will open a way to develop the materials inhibiting effectively migration by making the solid solutions of Ag and Cu with other metals.

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