Development of Copper Materials and Processing for Printed Electronics

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Abstract

New material technologies for screen printing electronics were studied. A novel conductive paste which can be metallized at 180°C under reactive gas condition was developed using needle-shaped copper compound particles without any dispersant, protective agents or binder resins. The obtained conductive trace of dense 1.5 μm thick Cu layer with a crystal structure showed the volume resistivity of 2.4 μΩ·cm and excellent reliability. The metallization mechanism and excellent electrical performance were concluded to be different from those of the sintering.

Keywords: Printed Electronics, Conductive Paste, Cu Paste, Screen Printing, Metallization

1. Introduction

Printed electronics is now attracting attention in various fields such as the fabrication of electronic circuits, organic transistors, displays and others, because of the simplified process which can reduce the amount of wastes and chemicals compared with the conventional photo mask process. Therefore new materials, such as conductive ink and insulator ink, have been studied for this new technology.[1, 2]

Silver and gold nano-particles were typically used as the metal source for the conductive ink in previous studies because of its air stability.[3, 4] These inks show low volume resistivity in spite of low sintering temperature. This is because higher surface energy of metal nano-particles decreases the process temperature, than bulk metals melting point. Recently, copper has been in the spotlight as the conductive material, because of the low volume resistivity, high reliability, and cost effectiveness compared with silver or gold. Several companies have reported the copper nano-particle inks.[5, 6] Most Cu inks contained dispersants or protective agents to avoid aggregations or oxidation of copper nano-particles, so they showed good preservation stability. In addition, several metallization methods at 200°C or higher were also studied. Most of these materials and processes provide necking structures, because the metallization mechanism occurs through low temperature sintering in which nano-metal particles merely gather.

As mobile devices in coming generations are desired to be lighter, thinner and more flexible, lower temperature metallization processes to use plastic film substrate have become increasingly important. We have reported about Cu ink and insulator ink for ink-jet printing and low temperature metallization processes for Cu ink so far.[7, 8] The Cu ink mainly consists of nano-sized copper compound particles and high boiling point solvent, and does not contain any dispersants or protective agents which require high temperature processing or oxidizing atmosphere to burn up organic substances. Using this Cu ink, a low resistive dense crystalline structural Cu layer which is similar to plated metal layer was generated at 185°C. These material technologies will be essential for the plastic devices of the next generation.

In this paper, a new Cu conductive paste for screen printing which provides the dense Cu layer with crystalline structure and the mechanism of low temperature metallization processes are reported. In addition, the reliability for electric devices is also reported.

2. Experimental Details

2.1 Cu paste

The Cu paste for screen printing mainly consists of submicron sized copper compound particles, a viscosity modifier and a high boiling point solvent. This paste does not contain any dispersants or protective agents as ink-jet ink reported in our previous studies. Three different shapes of
copper compound particles, spherical-, needle- and plate shape, were tested to develop the high printing performance paste.

2.2 Viscosity analysis

The viscosity of Cu paste was calculated based on the Casson flow equation (Equation (1)). It is well known that it can describe the flow behavior of thick dispersal systems such as a printing paste, a paint and so on. The stress against to the shear rate was measured by a cone-plate viscometer.

\[ s^{1/2} = s_c^{1/2} + (\mu_c \cdot D)^{1/2} \]

where:
- \( s \); Shear stress
- \( s_c \); Casson yield value
- \( \mu_c \); Casson viscosity
- \( D \); Shear rate

2.3 Screen printing

A screen printing was performed at 25°C in a temperature-controlled room. The printing was carried out with 310 (polyester) or 640 (metal) mesh screens using a hand-printing machine. The Cu paste was printed on poly (ethylene naphthalate) (PEN) film, and then the printed samples were dried at 150°C for 10 minutes.

2.4 Metallization process

(A) Metallization by reactive gas

The printed samples were set on a heat stage in a N\(_2\) atmosphere chamber. Then, the stage was heated up to 180°C of the sample temperature. The samples were kept heated at 180°C for 30 minutes with a reactive gas flow. The thickness of the conductive trace was approximately 1.5 \( \mu m \).

(B) Metallization by atomic hydrogen

The printed samples were treated with atomic hydrogen generated on a heated tungsten wire at a temperature of 1800°C in a hot wire (HW) apparatus in a vacuous chamber (Fig. 1). The temperatures of the samples were lower than 50°C during the metallization.

2.5 Reliability test

A thermal cycle (TC) test was carried out to test the connection reliability of the conductive trace. The conditions and sample structure are shown in Table 1 and Fig. 2. Writing resistance was measured before and after the test treatment indicating structure change and oxidization of the traces.

2.6 Observation of cross sectional image

The cross sectional images were observed by a focus ion beam/scanning ion microscopy (FIB/SIM; Hitachi FB-2000A). Cross sectional specimens of the Cu traces were prepared using a focused ion beam (FIB) micro-sampling technique which was operated at the acceleration voltage of 30 kV with Ga+ ion source. Before the FIB treatment, the surface of the Cu trace was coated with Pt and W to protect the generation of the oxide layer.

3. Results and Discussion

Scheme 1 shows the normal process steps to fabricate the conductive trace using our material. The black Cu paste is printed on a substrate using a screen printing machine. Then the printed Cu paste is metallized after the drying process. After the metallization, the color of the pattern changes to bronze and an electrical conductivity is imparted. The maximum temperature is below 180°C through the process. So, it is applicable to the organic substrates such as epoxy, polyimide (PI), PEN, and so on.

3.1 Properties of Cu paste

Generally, the rheology control of the paste would be the key factor to print fine patterns. Many kinds of additives such as binder resins are commonly used to control the paste rheology. However, when the additives are contained in the paste, conductive properties may be worsened and a higher temperature treatment may also be needed for metallization. Therefore, we tried to control the rheology by the particle shape of the copper compound.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>TC test condition.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Item</td>
<td>Condition</td>
</tr>
<tr>
<td>Temperature/time</td>
<td>-55°C/15 min ⇔ 125°C/15 min</td>
</tr>
<tr>
<td>Cycle number</td>
<td>100 cycles</td>
</tr>
</tbody>
</table>

![Fig. 1 Hot wire apparatus.](image)

![Printed conductive trace](image)

Electrode (Cu foil)  Insulator ink (for under and over coat)  Substrate (Glass/ epoxy laminate)
particles.

The Cu pastes using three different shape (spherical-, needle-, plate-shaped) copper compound particles were prepared. Table 2 shows the comparison of Cu particles in the pastes. The printing was carried out with a 310 mesh screen. As shown in the Table 2, Cu pastes using the spherical- or the plate-shaped particle showed poor print results compared with the paste using the needle-shaped particle. The preservation stabilities of the pastes with the spherical- or needle-shaped particles were relatively good.

We speculated that the contact area affects the adhesion strength of particles, so the plate-shaped particles which have large contact area aggregate easily. On the other hand, spherical- and needle-shaped particles which have the smaller surface attraction force among particles achieved uniform dispersion in the paste and slower sedimentation of the particles. Thus, the needle-shaped particle was chosen as the best copper compound particles candidate.

Figure 3 shows the results of a screen print using the optimized Cu paste of needle-shaped particles. The screen printing was carried out with a 640 mesh screen. The fine pattern of L/S = 70/30 μm in different angles were printed with the new Cu paste. The feature of the developed Cu paste is summarized in Table 3.

3.2 Low temperature metallization

Figure 4 shows the photographs of screen printed Cu paste pattern on PEN film before and after the metallization by reactive gas of method (A), mentioned before. The black color of Cu paste pattern changed to bronze after the metallization. The volume resistance of the metallized Cu

<table>
<thead>
<tr>
<th>Item</th>
<th>P1</th>
<th>P2</th>
<th>P3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle shape</td>
<td>Spherical</td>
<td>Needle</td>
<td>Plate</td>
</tr>
<tr>
<td>SEM image of copper compound particle</td>
<td><img src="image1" alt="SEM image" /></td>
<td><img src="image2" alt="SEM image" /></td>
<td><img src="image3" alt="SEM image" /></td>
</tr>
<tr>
<td>Screen printing result (L/S = 100/100 μm)</td>
<td><img src="image4" alt="Screen print result" /></td>
<td><img src="image5" alt="Screen print result" /></td>
<td><img src="image6" alt="Screen print result" /></td>
</tr>
<tr>
<td>Preservation stability</td>
<td>Good</td>
<td>Good</td>
<td>Bad</td>
</tr>
</tbody>
</table>

Table 3 Properties of Cu paste.

<table>
<thead>
<tr>
<th>Item</th>
<th>Cu paste</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paste</td>
<td>Copper compound</td>
</tr>
<tr>
<td>Solid content</td>
<td>50–70%</td>
</tr>
<tr>
<td>Viscosity</td>
<td>3–4 Pa·s</td>
</tr>
<tr>
<td>Temperature of process</td>
<td>180°C</td>
</tr>
<tr>
<td>Conductive layer</td>
<td>Volume resistivity</td>
</tr>
<tr>
<td></td>
<td>2.4–8.1 μΩ·cm</td>
</tr>
<tr>
<td></td>
<td>Thickness</td>
</tr>
<tr>
<td></td>
<td>0.5–1.5 μm</td>
</tr>
</tbody>
</table>

Fig. 3 Results of fine patterns printed in different angles.
pattern was 2.4 $\mu\Omega\cdot\text{cm}$, which is only 1.5 times higher than that of the bulk copper (1.7 $\mu\Omega\cdot\text{cm}$). Figure 5 shows a cross sectional image of 1.5 $\mu\text{m}$ thick Cu layer. As shown, a dense Cu layer with crystalline structure without any void was clearly formed.

Figure 6 shows the change in the cross sectional image of the printed pattern during the metallization process. Only submicron-sized copper compound particles were observed at the beginning of the metallization. After five minutes lapse metallization, the nuclei of copper crystal began to be observed at the interface between the substrate and the Cu paste. From this point, the crystals continued growing until they formed a dense crystalline layer of 1.5 $\mu\text{m}$ thick. However, the nuclei formation also occurred in the middle of the copper paste resulting in forming a porous layer on the dense copper layer. Therefore the maximum growth thickness of Cu layer was around 2 $\mu\text{m}$.

We assumed that the heated substrate activated the reaction of copper compound and reactive gas at the interface, resulting in initializing the nucleation. Therefore, a dense Cu layer may grow from the surface of the substrate at a low temperature. It seems that the metallization feature of our materials is different from sintering. In the case of sintering, a temperature higher than 200°C is needed to burn up the organic substances in high temperature and particles merely gather with high surface energy resulting in the partial connection of the necking structure with voids.

### 3.3 Electrical reliability

Two types of Cu trace made by the different metallization methods were compared for the TC test. One was the dense Cu trace with a crystalline structure ((A), metallization by reactive gas) and the other was the necking structure Cu trace with voids ((B), metallization by atomic hydrogen).

As shown in Table 4, both samples showed no disconnection after the test treatment. The change rate of wiring resistance of the printed conductive trace (A) was only 8% after 100 cycles of TC test despite the fact that the trace thickness was 0.2 $\mu\text{m}$. On the other hand, the resistivity of trace (B) was very high and became ten thousand times higher than the initial after the TC test. The poor reliability of trace (B) may come from the necking structure layer with large surface area which can easily oxidize. Therefore, the dense structure of trace (A) may be the favorable one.

Figure 7 shows cross sectional images of (A) after 1000 cycles of the TC test. The oxidized layer was formed on the surface of Cu trace, which was not found before TC test. The average thickness of this oxidized layer was 35
The oxidation caused a raise in resistance. We assume that the changing rate of resistivity of Cu trace may improve with the increasing thickness of the trace, suggesting the potential need of Cu trace.

4. Conclusion

We have developed conductive Cu paste for printed electronics, especially for screen printing. The rheology and the preservation stability of the paste were controlled by the particle shape of copper compound without any additives or dispersants. The Cu paste using needle-shaped particles showed good preservation stability and printability.

Low temperature metallization processes and the electrical reliability of the Cu trace were also studied. Dense Cu layer with a crystal structure was formed using Cu paste and the novel low temperature metallization process. The maximum thickness of the conductive trace was 1.5 μm. The volume resistivity was 2.4 μΩ·cm which is only 1.5 times higher than that of the bulk copper.

Based on the observations of cross sectional images of growing Cu layer, the metallization mechanism was thought to be different from sintering. Furthermore, the connection reliability of dense Cu trace was excellent compared to sintered one.

![Oxidized layer](image)

Fig. 7 Cross sectional image of Cu layer after 1000 cycles of TC test.

<table>
<thead>
<tr>
<th>Item</th>
<th>Metallization method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(A) Crystalline growth</td>
</tr>
<tr>
<td>Metallization Source</td>
<td>Reactive gas</td>
</tr>
<tr>
<td>Structure</td>
<td>Crystalline/Dense</td>
</tr>
<tr>
<td>Cu trace</td>
<td>Cross sectional image</td>
</tr>
<tr>
<td></td>
<td><img src="image" alt="Cross sectional image" /></td>
</tr>
<tr>
<td>Initial resistivity</td>
<td>0.1 Ω</td>
</tr>
<tr>
<td>Disconnection</td>
<td>None</td>
</tr>
<tr>
<td>Change rate of resistivity</td>
<td>+ 8%</td>
</tr>
</tbody>
</table>

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Table 4  Results of TC test.

References


