[Short Note]

Material Technology of Conductive Wiring for Ink-jet Print

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Abstract

New material technology for ink-jet printing has been studied. The relationship between new insulator ink and conductor ink was investigated. The fine pattern with highly adhesive performance was obtained by the simple process without any photomask. Experimental results revealed that the contact angle and the sliding angle are important parameters. The insulator ink was used for the insulating, surface leveling and material adjusting between the conductive traces. The new metallization process to fabricate the conductive copper trace was also investigated. The temperature of the process was below 200°C, which is suitable for organic substrates. The volume resistivity and pull-strength testing showed that the developed inks are applicable to fabricate highly conductive, smooth and straight patterns.

Keywords: Printed Electronics, Ink-jet Process, Copper Wiring, Insulator Ink, Conductor Ink

1. Introduction

Ink-jet printing technologies popular in both the home and the office have lately been used in the mass production of many industrial devices. They include displays and electronics,[1, 2] and are expected to grow rapidly.

Compared to a conventional photomask process, the ink-jet printing can reduce numbers of process steps and amounts of waste. In the conventional process, a copper foil is used as a starting material. The surface of the copper foil is coated or laminated with an etch resist. Then, the resist is patterned by exposure using a photomask, followed by post-baking and removing unnecessary portion. After the resist is patterned, the copper foil is removed by chemical etching. Thus, a large amount of waste and chemicals are discharged from the conventional process.

In contrast, the ink-jet process is simple and efficient. There are only three steps. First, a conductor ink is printed onto a target position of substrates. And then it is dried and finally, metallized. The ink-jet process is eco-friendly, and has advantage in changing the patterning design. It can be changed easily on a computer with CAD data.

There is a demand of developing new materials for fabrication of new structures in many electronics applications such as the three dimensional (3D) structures which are the alternate material of wire-bonding and the next-generation package on package (PoP) structures[3, 4] that have the added bonus of enabling printed traces on non-flat surfaces.[5] Some of the previous studies for the ink-jet printing electronics were concerned with the ink-shedding treatment between conductive patterns and preparing the ink-absorbing layer before printing, though increasing steps of the process.[6]

On the contrary, combining our newly developed insulator ink and conductor ink, we can form intended shapes of trace pattern without the ink-shedding treatment or preparing of the ink-absorbing layer. In this study, we discuss the insulator ink used as the interlayer material, which ensure the smooth surface and sufficient adhesion, between the conductor ink and the boards.

2. Materials and Methods

2.1 Insulator ink and conductor ink

The insulator ink used the thermosetting low-molecular-weight resin system commonly has used for glass cloth/epoxy laminate. Viscosity of insulator ink was prepared 8 to 12 mPa·s with solid content from 25 to 28 mass percent in this study.[7] The low-molecular-weight resin is suitable for preparing low viscosity and high solid content ink. In addition, it shows the excellent electrical reliability and high heat resistance because it constructs highly cross-linked structure after curing. The ink contained high-boiling-point solvents to prevent ink-jet nozzles clogging and a
small amount of surface conditioner to form smooth surface. As the result, the surface tension was from 23 to 28 mN/m.

The conductor ink contained nano-sized copper-compound particles and high-boiling-point solvents. The particles were 75 nm in average diameter and covered with an oxidized layer. The viscosity of the conductor ink is from 8 to 12 mPa·s by adjusting solid content from 26 to 28 mass percent, and the surface tension is from 40 to 50 mN/m. The ink does not contain any dispersants which require a high-temperature processing or oxidizing atmosphere to burn up organic substances.

Generally, dispersion of nano-particles is difficult due to large molecular attraction when their diameter is smaller than around 20 nm.[8, 9] On the other hand, when the particles are from 50 to 100 nm in diameter, magnitude of the attraction is decreased. In addition, the oxidized layer can help the particle dispersing. It is less active than pure copper surface and more preventable of aggregation. In this study we fabricated well-dispersed conductor ink without dispersants according to these theoretical concepts.

2.2 Method for evaluation of ink properties

The viscosity was measured at 25°C by using a sine-wave vibro viscometer (SV–10, A&D Co., Ltd.). The surface tension was determined by the Wilhelmy plate method using a surface tensiometer (CBVP–Z, Kyowa Interface Science Co., Ltd.). The particle size was measured with a laser diffraction particle size analyzer (LS13–320, Beckman Coulter Inc.). The properties of insulator ink and conductor ink are shown in Table 1.

2.3 Ink-jet printing

The inks were printed using an ink-jet printer (Nano Printer–1000, Microjet Corp.) with a piezoelectric ink-jet head (orifice diameter: 38 µm).

2.4 Surface modification

The insulator ink was printed on substrates to make a flat and smooth surface (thickness: from one to 40 µm). After curing the insulator, a UV-dry processor (PL16–110A, Senengineering Co., Ltd.) was used to control the insulator surface condition.

2.5 Metallization process

The conductor ink was printed on the controlled insulator surface. The metallization process was performed after drying the ink. The sample of printed conductor on the insulator was set in the chamber purging N₂. Then, the chamber was heated until the temperature of the sample was 180°C. The sample kept heated at 180°C for 30 minutes with reductive gas flowing to metallize. The thickness of the copper trace was approximately 1 µm.

2.6 The surface shape of the insulator

The arithmetic-mean-roughness degree (Ra) of the materials was measured with a non-contact interference microscope profilometer (Vertscan 2.0, Ryoka Systems Inc.), and the printed shape was examined with a profilometer (XP–2, Ambios Technology Inc.).

2.7 Contact angles and sliding angles

Contact angles and sliding angles were measured using a contact angle meter with an automatic image analyze system (DM 500 with DM–SA01, Kyowa Interface Science Co., Ltd.). The sliding angle is angle between surface and horizontal direction when the droplet on the surface just starts moving during the surface inclining little by little.[10]

2.8 Adhesion strength

Adhesion strength between the insulator layer and the conductive trace was measured with a pull strength tester (Romulus, Quad Group Inc.). The sample was prepared by attaching a stud pin to the conductive trace (shown in Fig. 1).

![Fig. 1 The pull-strength test apparatus.](image)

| Table 1 Properties of insulator ink and conductor ink. |
|---------------------------------|----------|------------|-----------------|
| Item                           | Unit     | Insulator ink | Conductor ink   |
| Main materials of solid fraction | –        | Epoxy resin  | Copper compound/copper oxides |
| Solid content                  | mass%    | 25–28        | 26–28           |
| Viscosity (at 25°C)            | mPa·s    | 8–12         | 8–12            |
| Surface tension                | mN/m     | 23–28        | 40–50           |
| Average diameter of particles  | nm       | –           | 75              |
2.9 Storage elastic modulus

Storage elastic modulus was measured by dynamic mechanical analysis (RSA3, TA Instruments Inc.). The sample length, width and thickness were 20, 5 and 0.5 mm, respectively. Measurement frequency was 1 Hz and heating velocity was 5°C per minute.

3. Results and Discussion

3.1 Leveling of surface asperity

The insulator ink was able to form the flat surface with Ra of 0.06 µm on an encapsulant (Ra 1.70 µm). The scanning electron microscopy (SEM) images before and after printing the insulator are shown in Fig. 2. The insulator ink could also make slopes on stepped sections of stacked chips. The original height of the step was assumed to be 35 µm, the sum of the thicknesses of chip and die-bonding material. The slope between the chip and the substrate created by the printed insulator is shown in Fig. 3.

3.2 Patterning characteristics of inks

It is important to define the interfacial characteristics between the printed insulator and the conductor ink for making smooth and straight-lined traces.[11] We investigated the characteristics using the contact angle and the sliding angle of the droplet on the insulator. The solvent of the conductor ink was used as the droplet on the insulator under various surface conditions. Pictures of the printed trace on the insulators are shown in Fig. 4. The sliding angles are plotted against the contact angles as shown in Fig. 5.

Fig. 2 SEM image of the encapsulant surface before and after printing the insulator. (a) Original surface (Ra = 1.70 µm). (b) After printing (Ra = 0.06 µm).

Fig. 3 Cross-sectional profile of the stacked chip on the substrate. (a) Without the printed insulator (dashed line). (b) With the printed insulator (solid line).

Fig. 4 Picture of the printed trace on the insulators.

Fig. 5 Dependence of the patterning characteristics on the contact angles and the sliding angles of the ink solvent (the graph legends are same to the pictures in Fig. 4).

Fig. 6 Relationship between interfacial condition and patterning characteristics.
Fig. 5. The interfacial effects of the patterning characteristics are shown in Fig. 6.

The contact angle is a well-known parameter of wetting. It is predicted that the straight line tend to be obtained when the contact angle is small. However, the dashed line was also obtained in the condition of same contact angle. It indicated that another factor influenced this phenomenon. We introduced sliding angle as the second parameter, which can be used as mobility of the droplets.

The sliding angle reflects whether the surface is ink-removable or ink-attaching. If the surface is ink-removable, the sliding angle is small and the adjacent droplets tend to gather each other because of their surface tension.

The printed results in Fig. 5 indicated that the ink-attracting and ink-attaching surfaces were needed to print straight lines. On the other hand, the ink-shedding and ink-removable surfaces caused problems such as bulges or dashed lines. Therefore, both the contact angles and the sliding angles on the insulator surface were used as the practical parameters of the interfacial interactions as shown in Fig. 6.

### 3.3 Resistivity and adhesion of copper trace

Table 2 shows the storage elastic modulus (G') of the insulators at 180°C, adhesion strength (pull strength) and volume resistivity of conductive traces after metallization. The typical appearance of the trace is shown in Fig. 7. Transmission electron microscope (TEM) and the cross-sectional images of the scanning ion microscope (SIM) are shown in Figures 8 and 9, respectively.

The conductive trace showed low volume resistivity of 2.4 \(\mu\Omega\text{-cm}\) on the glass, but its pull strength was poor. On the other hand, the pull strength on the insulators was improved. The values were 4 and 18 MPa on insulator A and B, respectively.

The storage elastic modulus, \(G'\), was considered as the key factor for the behavior of the pull strength. \(G'\) of insulator A at 180°C was 700 MPa and that of B was 10 MPa. If \(G'\) is large like the insulator A, the insulator tends to be undeformable. In contrast, if \(G'\) is small enough like the insulator B, the insulator could deform following the trace shape during metallization treatment at 180°C to increase the contacting interface between the insulator and the conductive trace.

As shown in Fig. 8, the insulator B well followed the con-

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<th>Table 2</th>
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<td><strong>Item</strong></td>
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<td>Storage elastic modulus of the insulator ((G')) at 180°C</td>
<td>MPa</td>
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<td>Pull strength</td>
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<td>Volume resistivity</td>
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ductive trace, and the copper crystalline component of the conductive trace on the contact interface tended to penetrate the insulator.

The volume resistivity of the trace on the insulator B was 3.4 $\mu\Omega\cdot$cm which is as low as double of the pure copper, 1.7 $\mu\Omega\cdot$cm. It was indicated that the ink traces on the insulator become conductive at the temperature lower than 200°C, suggesting that the traces without any organic dispersant forms the dense and continuous metallic structure.

The metallization process is intended for following. At first, the reductive gas reacts with the copper particles. Next, the product of the reaction is deposited on the substrate like as chemical vapor deposition. As the result, the dense and continuous structure of copper layer is obtained. The suggested result agreed with the observed result in Fig. 9.

4. Conclusion

We developed the insulator ink that works not only as an insulator between conductive traces but also as a surface leveling material. It can make the smooth surface (Ra: 0.1 $\mu$m or less), and the smooth slope at the step of 35 $\mu$m height. The surface of the printed insulator layer was characterized by the contact angle and the sliding angle. Controlling the values of two parameters, the straight-line trace patterns without any bulges or breaks were formed. The volume resistivity of the copper trace was 3.4 $\mu\Omega\cdot$cm and the adhesive strength between the insulator and the conductor was 18 MPa.

These results suggest that the newly developed inks are applicable to the on-demand and 3D wiring on rigid or flexible substrates. Our current target of thickness of the copper trace is 5 $\mu$m or more with adequate mechanical strength to introduce the all-ink-jet process for fabricating printed-wiring boards.

References