Two-Step Reduction Process for Direct-Metallization

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Abstract
Flexible Printed Circuits (FPCs) have been commonly utilized for electric gadgets such as Liquid Crystal Displays (LCDs). Direct-Metallization is a promising method for plating highly conductive copper onto the polyimide films when fabricating the FPCs. In this paper, we suggest a two-step reduction process to improve the adhesion between the polyimide film and the precipitated copper metal with an enhanced mechanical interlocking effect. The peel strength of the metalized polyimide-based film is improved from 0.3 to 0.8 kN/m by adopting this process. Observation of the boundary structure between the copper metal and polyimide film reveals that the precipitating small and uniformly-sized copper particles are distributed just below the surface of the polyimide.

Keywords: FPC, Substrate, Direct-Metallization, Surface-Modification, Polyimide, Copper

1. Introduction
In the field of electronic device applications, Flexible Printed Circuits (FPCs) consist of metallic patterns and dielectrics such as Liquid Crystal Displays (LCDs), which have been commonly utilized for downsizing. One promising candidate for dielectrics is polyimide, which offers good thermal stability, chemical stability, and mechanical and dielectric properties. Further, copper is a useful metal owing to its high electrical conductivity and excellent electro-migration resistance.

We have studied a novel method for fabricating FPCs which involves modifying the polyimide surface. The method is called Direct-Metallization, and is useful in terms of process simplicity. The following is a brief description of the overall process of Direct-Metallization. First, a bare polyimide film is treated with an alkali solution for cleaving the imide rings of the polyimide near the surface with a hydrolysis reaction. Simultaneously, polyamic acid alkali salt forms. Subsequently, metal ions load into the modified-region, forming polyamic acid with the metal salt through an ion exchange reaction. The metalized polyimide-based film forms through chemical reduction of copper ions.[1, 2]

Finally, polyamic acid, which has a chemically unstable polymer structure, should transform to polyimide (through thermal re-imidization) after the polyimide-based film is metalized.

We previously reported that the residual copper ions and polyamic acid with metal salt interrupt the thermal re-imidization reaction.[3] At that time, we also indicated a method for removing the copper ions from the polyamic acid with metal salt. Nevertheless, the peel strength of 0.3 kN/m between the copper metal and polyimide-based film still remained a serious problem.[4]

In the present study, we report on the improvement of the adhesion between the polyimide-based film and the copper metal due to copper particles distributed just below the surface region of the polyimide film.

2. Experimental Section
The polyimide films used in this study were a 125 μm-thick biphenyl dianhydride-p-phenylene diamininate (BPDA-PDA) type. The procedure employed for Direct-Metallization is presented in Table 1. The procedure involves five steps: (i) surface modification of the polyimide using an alkali treatment, (ii) adsorption of copper ions into the modified region, (iii) reduction of copper salts to copper metal (the step is further divided into three sub-steps described
below), (iv) removal of residual copper ions from the modified region, (v) thermal re-imidization.

Step (iii) involves the three steps shown in Fig. 1 for precipitating a large amount of copper in the modified region. (iii (A)) soaking the sample in an aqueous solution of sodium tetrahydroborate (NaBH₄) at 10 degrees C to enhance the accumulation of BH₄⁻ ions by extending the lead time. (iii (B)) reduction of copper ions to copper nanoparticles by soaking in hot water. (iii (C)) reduction of copper ions for the growth of the copper nanoparticles.

The formation of the precipitated copper nanoparticles was investigated by Field Emission-Scanning Electron Microscopy (FE–SEM).

The following method was used for the observation:
(1) Observation of the cross-sectional structure.
(2) Observation of the surface morphology of the copper-etched modified region.

The adhesion between copper metal and modified region was examined with a 90° peel test after adding a 10 μm-thick copper layer by electroplating.

### 3. Results and Discussion

The volume of copper particles precipitated in step (iii) increases with increasing thickness of the modified region, which results in the improvement of the adhesion between the copper particles and the polyimide-based film. Thus, extending time of the alkali treatment in step (i) is probably preferable. Figure 2(b) shows an optical image of the polyimide film surface after 60 minutes of alkali treatment that reveals the occurrence of cracks in the modified region. It is assumed that the dissolution of the polyimide causes the reduction of bulk hardness. The alkali treatment time was set at 40 minutes because no cracks occurred on the surface of the modified region with this time.

Regarding step (iii), when extending the soaking time in step (iii (A)), the color of the film surface temporarily turns from brown to blue, and subsequently to a metallic color. This change to blue is considered to be due to the generation of hydrated copper in the modified region. On the basis of this assumption, the soaking time in step (iii (A)) was changed to 15 minutes before the turn to the metallic color.

Figure 3 shows cross-sectional SEM images for reduction times in step (iii (A)) of (a) 13.5, (b) 14.5 and (c) 15 minutes, compared with (d) one-step reduction. The small and uniformly-sized copper particles distribute

### Table 1 Bath composition and condition for Direct-Metallization.

<table>
<thead>
<tr>
<th>Step</th>
<th>Composition and Condition</th>
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<tr>
<td>(i) Alkali treatment</td>
<td>KOH, 5 mol/L, 40°C</td>
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<tr>
<td>(ii) Adsorption of copper ions</td>
<td>CuSO₄•5H₂O, 0.05 mol/L, 20°C, 60 minutes</td>
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<tr>
<td>(iii) Reduction of copper ions to metal particles</td>
<td>In case of two step: (A) NaBH₄, 1 mmol/L, lower than 10°C (B) Soaking in hot water (30°C) (C) NaBH₄, 1 mmol/L, 20°C In case of one step: NaBH₄, 1 mmol/L, 20°C</td>
</tr>
<tr>
<td>(iv) Removal of residual copper ions</td>
<td>NaOH, 1 mmol/L, 20°C, 3 minutes Citrate acid, 0.2 mol/L, 20°C, 7 minutes</td>
</tr>
<tr>
<td>(v) Re-imidization</td>
<td>350°C (with 4 step)</td>
</tr>
</tbody>
</table>

Fig. 1 Flow chart for the reduction process.

![Fig. 1 Flow chart for the reduction process.](image)

![Fig. 2 Optical images of the polyimide-based film surfaces before & after alkali treatment.](image)
in the modified region for condition (a). It is assumed
that the copper particles do not precipitate excessively in
step (iii (A)), which suppresses the growth of those par-
ticles.

In contrast, for conditions (b) and (c), cracks occur on
the surface of the modified region and cause a split
between the modified region and the mass of copper parti-
cles. This result can be attributed to the large and nonuni-
formly-distributed particles causing stress concentration
points. Varying the lead time for the accumulation of BH$_4^-$
ions affects their boundary structures. Consequently, the
reduction time in step (iii (A)) resulted in less than 14.5
minutes when referring to the other conditions in Table 1.

To understand the structure of the copper precipitation
in the modified region in more detail, the surface morphol-
ogy of the modified region on the samples was observed
after etching the copper metal with HCl. Figure 4 shows
the surface morphology for reduction times of step (iii(A))
of (a) 13.5 and (b) 14.5 minutes. The substantial holes
formed in the modified region correspond to areas where
copper particles had precipitated in Figs. 4(a) and (b).

The copper particles distributed in the modified region
for the reduction step (iii (A)) time of 13.5 minutes are
small and uniformly sized compared with those for the
time of 14.5 minutes. This result is in good agreement with
the observation of the cross-sectional SEM images in Fig.
3(a) and (b). Therefore, the reduction time in step (iii (A))
was set at 13.5 minutes.

The temperature for the hot-water bath in step (iii (B))
was set at 30 degrees C, which resulted in no damage to
the modified region. In addition, soaking in hot water pro-
duced favorable results in the time range from 1 to 5 min-
utes before the dissolution of the precipitated copper metal. Therefore, the soaking time in step (iii (B)) was
fixed at 3 minutes.

Subsequently, the reduction time in step (iii (C)) was
fixed at 50 minutes, considering the risk of damage to the
modified region.

Figure 5 shows the surface morphology observed from
samples for the two-step reduction (iii(A)) time of 13.5
minutes and one-step reduction after etching of copper
metal with HCl. The density of the nano-sized holes for
the two-step reduction is higher than that for the one-step
reduction. Therefore, the density of the distributed copper
particles in the modified region significantly increase with
adoption of the two-step reduction. In addition, observation
from the cross-sectional SEM image in Fig. 3(a) reveals
that the precipitated copper structure of the two-step
reduction has a higher density of copper particles in the
modified region than that of the one-step reduction shown
in Fig. 3(d). As a result, the formation of those copper par-
ticles is ideally structured in the modified region with the
two-step reduction.
Figure 6 shows the peel strength obtained from the samples for the two-step reduction with reduction step (iii (A)) times of 13.5 minutes and 14.5 minutes, and that for one-step reduction.

The peel strength for two-step reduction is drastically improved, from 0.3 to 0.8 kN/m (for the reduction time of 13.5 minutes in reduction step (iii (A))). This is in good agreement with the observation of the surface morphology and the cross-sectional images. It is clarified that the two-step reduction contributes to the ideal formation of the copper precipitation and thus to the improvement of the adhesion between the copper metal and the modified region. On the other hand, the peel strength with a reduction time of 14.5 minutes in reduction step (iii (A)) is nearly the same as that of the one-step reduction. This can be attributed to the overgrowth of copper nanoparticles in the modified region, causing the decrease of the anchor effect.

4. Conclusion
A two-step reduction process improves the adhesion between the polyimide-based film and the precipitated copper metal with an enhanced mechanical interlocking effect. Extending the lead time for the accumulation of BH₄⁻ ions in the modified region allows the precipitation of small and uniformly-sized copper particles.

By adopting this process, the peel strength of the metallized polyimide-based film is improved from 0.3 to 0.8 kN/m. Observation of the boundary structure between the copper metal and polyimide films reveals that small and uniformly sized copper particles are distributed in the modified region. It also revealed that the reduction time in step (iii (A)) should be less than 14.5 minutes to obtain the ideal copper structure.

References