Electroless Copper Deposition on Polyimide Substrate Using Hypophosphite as a Reducing Agent
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Abstract:
Commercial electroless copper plating baths usually use formaldehyde (HCHO) or its derivatives as the reducing agents. Formaldehyde is a carcinogen that potentially release hazardous gases during operation. Thus, an environmental-friendly electroless copper plating using hypophosphite has been investigated. However, the oxidation of hypophosphite is not automatically catalyzed by deposited copper. The method to catalyze the oxidation of hypophosphite is activated substrate by adsorbed palladium the added nickel ions into the bath. In this work, we compared the surface morphology and composition between the deposition with palladium-based seed catalyst and palladium mixed in the electroless solution and studied the effect of nickel concentration and temperature. The SEM/EDS results showed that copper deposits were more uniformly distributed on the palladium-seeded sample with contained less nickel and palladium contamination than the sample in palladium-mixed solution. And when increased NiSO₄ concentration the copper content slightly increased and nickel content greatly increased. In addition, the particle size of copper depositions increased with increased NiSO₄ concentration and temperature.

1. Introduction
Nowadays, the electronic device such as mobile phone, computer and high-performance devices has become more important in daily life. These devices require printed circuit board (PCBs) and an Integrated circuit (IC). Moreover, there has been an increase in demands of wearable electronics device such as smart watch, activity tracker and medical measurement device. These devices consist of flexible surface that in turn required flexible printed circuit board (FPCB). Besides the shape-changing surface, light weight, compact space, and low cost are also required for use in these portable devices.

A typical FPCB composes of four layers: the base layer (dielectric film/flexible substrate), metal foil or conductive layer, (optional) adhesive layer and cover layer. Polyimide (PI) films generally used as a base layer of FPCB because it has high thermal and chemical stability, low dielectric constant, transparency and flexibility. Copper has high electrical conductivity, with lower cost than silver. So, copper is commonly used as conductive layer in FPCB. However, polyimide does not have polar functional group, resulting in poor adhesive strength of polyimide film to copper deposit. To improve the adhesion, we need to functionalize the surface to make surface active.

Fabrication of conductive copper patterns on flexible substrates can be performed via many methods including selective electroless plating. Electroless deposition of copper is attractive for FPCB fabrication because it produces high selectivity, uniform thickness, uniform physical and mechanical properties film. In addition, the cost of tools and materials are low.
Commercial electroless copper plating baths usually use formaldehyde (HCHO) or its derivatives as reducing agents. However, formaldehyde baths have to operate at high pH and potentially release hazardous gases. Recently, some researchers interested in environmental-friendly electroless plating so they had studied electroless copper plating bath using non-formaldehyde such as dimethyl borane (DMAB), Sodium hypophosphite (NaH$_2$PO$_2$) and glyoxylic acid (CHOCOOH) as reducing agents.

Sodium hypophosphite has gained a lot of attention because it can be operated safely at low pH, low temperature, and low cost. However, the electroless copper plating process that uses hypophosphite as a reducing agent is more complex because copper cannot catalyze the oxidation of hypophosphite. Adding nickel ions to the bath for catalyzing the oxidation of hypophosphite. Nickel acts as a catalyst in the oxidation of hypophosphite resulting in the continuous copper deposition. However, the addition of nickel can result in a co-deposition of nickel in copper depositation, which reduces the conductivity of the copper layers. Another method is activated the substrates by the adsorption of palladium. Palladium is a good catalyst to activate the electroless deposition despite its high cost and possibility to contaminate the plating solution. In this work, we compare the surface morphology and composition between the deposition on palladium-based seed catalyst and the deposition with Pd mixed in the electroless solution. And we also find the optimum condition and study effect of NiSO$_4$ concentration and temperature for electroless copper plating using sodium hypophosphite as a reducing agent with a palladium-seed catalyst to achieve proper characteristics such as high uniformity, and good surface coverage.

2. Materials and Methods

2.1 Materials

In this study, 2.5 x 2.5 cm Polyimide film were used as substrates for electroless copper plating. The chemicals, copper sulfate pentahydrate (CuSO$_4$.5H$_2$O), Sodium hypophosphite (NaH$_2$PO$_2$.H$_2$O), Sodium hydroxide (NaOH) and Potassium hydroxide (KOH) were purchased from Carloerba reagents. Nickel sulfate (NiSO$_4$.6H$_2$O) was purchased from Kemaus. Sodium citrate (Na$_3$C$_6$H$_5$O$_7$) and Boric acid (H$_3$BO$_3$) were purchased from Ajax Finechem. Palladium chloride (PdCl$_2$) were purchased from Aldrich chemicals. All chemicals are in analytical grade.

2.2 Experimental Method

Polyimide (PI) sheets with a thickness of 0.25 mm and an area of 2.5x2.5 cm were used as substrates. Before electroless plating, the substrate was cleaned by immersion in acetone solvent for 15 minutes, then ethanol for 15 minutes, under sonication at room temperature. Following the solvent cleaning, the substrate was then dried under N$_2$ blow.

Before electroless plating, the sample were immersing in a 0.5 g/l PdCl$_2$ and 20 ml/l 38% HCl solution at room temperature for 10 min and then rinsed thoroughly under deionized water to avoid contamination from the plating bath. Then, the sample was continuously submersed in electroless copper plating bath. The chemicals composition of this plating bath is shown in Table 1. The palladium mixed in electroless solution carried out by dropped 0.4 ml of 0.5 g/l PdCl$_2$ and 20 ml/l 38% HCl into the electroless bath.

2.3 Analytical Method

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The surface morphology of the copper deposition was determined by scanning electron microscope (SEM) and the chemicals composition was measured by an energy dispersive x-ray (EDX).

### Table 1. The composition and operating condition of electroless copper plating bath

<table>
<thead>
<tr>
<th>Bath composition</th>
<th>Operating condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuSO$_4$.5H$_2$O</td>
<td>8 g/l</td>
</tr>
<tr>
<td>NaH$_2$PO$_3$.H$_2$O</td>
<td>30 g/l</td>
</tr>
<tr>
<td>NiSO$_4$.6H$_2$O</td>
<td>1.15.2 (g/l)</td>
</tr>
<tr>
<td>Na$_3$C$_6$H$_5$O$_7$</td>
<td>15 g/l</td>
</tr>
<tr>
<td>H$_3$BO$_3$ (M)</td>
<td>0.5</td>
</tr>
</tbody>
</table>

The SEM results in Figure 2 showed that copper depositions were more uniformly distributed on the palladium-seeded sample with relatively uniform size distribution and smaller nucleation size than palladium mixed in electroless solution sample. Moreover, the electroless bath with palladium mixed has very high nucleation growth resulting in good adhesion.

### Table 2. %weight of chemical content on the copper deposition at the same operating conditions.

<table>
<thead>
<tr>
<th></th>
<th>P</th>
<th>Ni</th>
<th>Cu</th>
<th>Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd-mixed</td>
<td>4.70</td>
<td>29.21</td>
<td>65.47</td>
<td>0.62</td>
</tr>
<tr>
<td>Treated Pd</td>
<td>2.58</td>
<td>17.71</td>
<td>79.64</td>
<td>0.07</td>
</tr>
</tbody>
</table>

### Figure 1. %weight of chemical content on the copper deposition.
3.2 Effect of NiSO\textsubscript{4} concentration

The composition of deposited films depended on the deposition conditions. It is noticed that the deposition rate without nickel ion is zero so the electroless plating using hypophosphite as a reducing agent could not occur without adding nickel ion. Nickel ion used as a catalyst for electroless copper plating, using hypophosphite as reducing agent, to catalyze the oxidation of hypophosphite. The compositions of the copper film from using various nickel concentrations bath are shown in Figure 3. The results showed that in all three cases only small amount of nickel and phosphorus and higher copper content were formed in the coating. According to the standard reduction potentials, shown in the following equations, copper is a better oxidizer than nickel so the Cu\textsuperscript{2+} could more easily receive electron from H\textsubscript{2}PO\textsubscript{2}\textsuperscript{-} than Ni\textsuperscript{2+}.

\[
\begin{align*}
\text{Ni}^{2+} + e^- & \rightarrow \text{Ni} ; E^0 = -0.25 \text{ V} \\
\text{Cu}^{2+} + 2e^- & \rightarrow \text{Cu} ; E^0 = 0.34 \text{ V}
\end{align*}
\]

When nickel concentration in the bath increased, the copper content slightly increased while nickel content greatly increased. Apparently, increasing nickel ion in the bath increased the nickel content in deposit. The electroless deposit also contained phosphorus from hypophosphite reduction. The oxidation reduction potential of phosphorus is lower than nickel and copper, resulting in the small phosphorus content. When increasing NiSO\textsubscript{4} concentration, hypophosphite was further oxidized by Ni\textsuperscript{2+} resulting in decreased phosphorus content.

The nuclei size was investigated by EDX. It is indicated that the particle size increased when increasing NiSO\textsubscript{4} concentration as shown in Figure 4 because when increasing NiSO\textsubscript{4} concentration, the reaction rate increase and some particle aggregate to form larger granules. The surface morphology of the copper deposited from different nickel concentration bath was shown in Figure 5. The high nickel concentration led to rapid nucleation,
resulting in high nucleation density and large grain size.

**Figure.4** Average nuclei size at difference nickel concentration.

### 3.3 Effect of bath temperature

Increasing bath temperature, the kinetics of reactions was more favorable, which enhanced the deposition rate, as observed from the reaction at high temperature start faster than at low temperature at the same conditions. The rapid deposition gave rise to better distribution and larger grain size of copper as presented in Figure 6.

**Figure.5** Surface morphology of the copper deposited from various nickel concentration A) 1 g/l, B) 1.5 g/l, C) 2 g/l with magnification X3500

### 4. Conclusion

The deposited copper catalyzed by palladium-based seed contained less contamination and has more uniformly distributed than mixed palladium in the electroless solution. Effects of deposition parameter such as NiSO₄ concentration and temperature on morphology and chemical composition of electroless copper plating on polyimide using hypophosphite as reducing agent were studied.
The result showed that when increased \( \text{NiSO}_4 \) concentration, the copper content slightly increased and nickel content greatly increased. In addition, the particle size increased as \( \text{NiSO}_4 \) concentration and temperature increased as indicated from the surface morphology of the copper deposition.

**Acknowledgements**

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**References**