A Wet Process for Forming an Adhesive Copper Layer on Polyimide Film

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A wet process for forming an adhesive Cu layer on polyimide (PI) film was developed. In this process, the surface of the PI film is pretreated in plasma, followed by the formation of a ligand-bearing organic layer of 3-aminopropyltriethoxysilane (APTES) molecules. After catalyzation with a solution containing Pd ions, thin layers of NiB as the underlayer and that of Cu as the conductive layer are deposited by electrodeless depositions, and then a 10 μm thick Cu layer is electrodeposited. The peel strength of the specimen prepared by this method was found to depend on the morphology of the NiB underlayer. A continuous NiB layer functions as a barrier layer that prevents Cu from contacting the PI film. In the presence of this efficient barrier layer, the peel strength was found to improve after annealing at 150 °C.

Key Words : Wet Process, Organic Layer, Adhesion Strength, Polyimide

1 Introduction

Flexible printed circuit boards are used in many electronic products such as mobile phones, digital cameras, and personal computers. Most of the circuit boards in these products are manufactured by pasting a polyimide (PI) film onto a Cu film, followed by patterning the circuits by the so-called subtractive method. The subtractive method is one of the processes to fabricate fine Cu line used in the printed circuit board.13 The Cu film provided on a substrate is covered with a lithographically patterned photoresist, and a wet chemical etch process is used to remove the unwanted Cu. As the downsizing of products progresses, the width of the circuit line and the space between the lines need to be made narrower. In the subtractive method, the minimum line width and space are, nowadays, 20 μm. Attempts have been made to form electric circuits with narrower lines and space by using electrodeposition methods.10

The high adhesion strength of the Cu wiring and the smoothness of the PI film surface are indispensable for the flexible printed circuits. The adhesion strength of the Cu wiring is, usually, obtained by the anchor effect. For future electronic products operated at higher and higher signal frequencies, the delay and decline of the signal are a significant problem, where the roughness being one of the reasons. The effect of smoothness of the interface between wiring and substrate becomes more pronounced at higher signal frequencies. It is required that high adhesion strength of Cu wiring is fabricated with maintaining the flatness of the original PI surface. Thus, it is significant to have available a technology for the electrodeposition formation of a Cu layer that strongly adheres to the surface of PI film without roughening it.

The authors previously proposed the all-wet process for producing Cu circuits in ULSI.1 In that process, an electrodeless NiB layer was used as a barrier against the diffusion of Cu atoms into the insulating layer. The NiB plating film was obtained using 3-aminopropyltriethoxysilane (APTES) as a catalyst immobilizing layer. The NiB plating film has a small grain size, good adhesion, and a diffusion barrier property superior to that of NiP, NiReP, NiWP, and NiWB plating films.6 The layer of NiB was deposited onto a catalyzed APTES layer5 on an oxidized Si surface.

In the present study, a similar process is used to form Cu wiring on PI film. This article discusses a wet process for forming an adhesive Cu layer on PI film.

2 Experimental

Polyimide film (Espanex MC15-40, Nippon Steel Chemicals Co., Ltd.) was used as the substrate. Plasma treatment was performed with a power of 200 W, for 30 sec in N2-Ar atmosphere to generate OH groups on the surface of PI film. The OH groups are necessary to attach organosilane onto the surface of the film. The PI film was immersed into a toluene solution of APTES (1 wt.%) for 10 min at 60 °C to form a layer of organic molecules. The specimen was catalyzed for 30 sec by immersing it into a solution containing 5.5 × 10−5 mol dm−3 PdCl2 and 0.01 mol dm−3 HCl. The metal films were formed by both electrodeless and electrodeposition methods. Electroless methods were used for fabricating the initial layer and the conductive seed layer. The state of the underlayer is considered to affect the adhesion strength
Table 1 Composition and operating conditions of electroless NiB plating solution.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiSO₄·6H₂O</td>
<td>0.1 mol dm⁻³</td>
</tr>
<tr>
<td>Citric acid</td>
<td>0.2 mol dm⁻³</td>
</tr>
<tr>
<td>DMAB *</td>
<td>0.05 mol dm⁻³</td>
</tr>
<tr>
<td>pH 9.0 adjusted with TMAH **</td>
<td></td>
</tr>
<tr>
<td>Bath Temperature 70 °C</td>
<td></td>
</tr>
</tbody>
</table>

* Dimethylamine borane  
** Tetramethylylamine hydroxide

Table 2 Composition and operating conditions of electroless Cu plating solution.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuSO₄·5H₂O</td>
<td>0.045 mol dm⁻³</td>
</tr>
<tr>
<td>EDTA †</td>
<td>0.09 mol dm⁻³</td>
</tr>
<tr>
<td>Glyoxylic acid</td>
<td>0.17 mol dm⁻³</td>
</tr>
<tr>
<td>2,2'-Bipyridyl</td>
<td>25 ppm</td>
</tr>
<tr>
<td>PEG † † 1000</td>
<td>750 ppm</td>
</tr>
<tr>
<td>pH 12.5 adjusted with TMAH</td>
<td></td>
</tr>
<tr>
<td>Bath Temperature 70 °C</td>
<td></td>
</tr>
</tbody>
</table>

† Ethylene diamine tetracetic acid  
† † Polyethylene glycol

Fig. 1 Schematic representation of the process used to form the Cu layer on PI film.

Fig. 2 Schematic illustrations of peel strength test.

of the Cu wiring. To verify this consideration, the conductive layer was formed by three types of methods. The compositions and operating conditions of the Ni alloy and the Cu electroless plating solutions are summarized in Table 1 and Table 2, respectively. A conventional Cu electroplating solution containing CuSO₄·5H₂O, H₂SO₄, HCl, polyethylene glycol 2000, and bis(3-sulfopropyl)disulfide, which is used in the damascene process, was used to obtain the thick Cu film. Figure 1 illustrates the schematic representation of the Cu film formation process used in this study. Annealing was performed in air for 1-96 hr at 150°C.

The surface state of the PI film before and after the plasma treatment was examined in terms of the contact angle of DI water (ERMA, G-1-1000) and by Fourier transform infrared spectroscopy (FT-IR, PerkinElmer, Inc., Spectrum One). Chemical characteristics of the modified surface were investigated using X-ray photoelectron spectroscopy (XPS, JEOL, JPS-9010TR) with a Mg Kα source. The surface roughness was studied by using an atomic force microscope. (AFM, Digital Instruments, Nanoscope III). Peel strength of the specimens with the annealing at 150°C was measured by the 90°C peel strength test (TOYOSEIKI, Strograph). The subtractive method was used to fabricate Cu lines for the peel strength measurements. The width of the lines was either 0.1 mm or 1 mm. Figure 2 illustrates schematic illustrations of the peel strength test.

3 Results and Discussion

3.1 Catalytic modification of PI film surface for electroless plating

The surface state of the PI film before and after the plasma treatment was examined in terms of the contact angle of DI water and by FT-IR. The contact angle of DI water on the PI film was measured before and after the plasma treatment. The contact angle before the plasma treatment was about 80 degrees; after the treatment it
was about 50 degrees. The surface state of the PI film before and after the plasma treatment was examined by using FT-IR. There is no characteristic peak for the OH group for the untreated PI film; however, a peak at around 3600 cm\(^{-1}\) was observed for plasma treated film, which indicates that plasma treatment generates OH groups on the surface of the film. This observation also was corroborated by the contact angle results.

XPS analysis of the PI film surface was performed to confirm the APTES layer formation and the catalyzation process. Figure 3 shows the XPS spectra of the Si(2p) region of the PI film surface. Figure 3-a shows that, with plasma pretreatment, an APTES layer has formed, whereas Fig. 3-b shows that, without plasma pretreatment, no APTES layer has formed. The binding energy value of 101.8 eV corresponds to Si(2p) of the APTES layer.\(^{12}\) The XPS results showed a pronounced peak at 101.8 eV for the plasma-treated PI film; however, there was no pronounced peak for the PI film that was not plasma treated, which indicates that the APTES layer was formed on the plasma treated PI film. These results show that plasma treatment is essential for the formation of an APTES layer.

Figure 4 shows XPS spectra of the Pd(3d) region of a Pd catalyzed surface with APTES layer (Fig. 4-a), and without APTES layer (Fig. 4-b). A peak at 337.3 eV was observed in the Pd with APTES, which means that the Pd presents in an oxidized state.\(^ {13}\) In addition, it means that the Pd ions exist in the form of hydroxo- Pd oligomers. This result is consistent with the finding reported by H. Kind et al.\(^ {11}\) In the subsequent process, immobilized hydroxo- Pd oligomers will be reduced to the metallic state by a reducing agent. These peaks assigned to Pd were not observed for film without an APTES layer (Fig. 4-b). This finding indicates that the APTES layer is necessary to immobilize Pd on the PI film. The Pd is considered to be immobilized by NH\(_2\) group of the APTES layer. As is clear in Figs. 3 and 4, the formation of an APTES layer is essential for immobilization of the Pd ions on the PI film.

The surface roughness of the modified PI film was observed by AFM. The average roughness value of the surface before and after the plasma treatment, after the formation of APTES layer, and after immobilization of the Pd ions on the APTES layer were 2.1, 1.3, 1.7 and 1.2 nm, respectively, showing that the smoothness of the surfaces remained unchanged after each step, relative to the usual method used to roughen Cu wiring. The scanned area was 1 \(\mu\)m square, and the Z-range (black to white) was 80 nm in this measurement.

These results confirmed the formation of the organic layer of APTES on the plasma-treated PI film surface and the immobilization of hydroxo- Pd oligomers on the APTES layer.

3. 2 Electroless-deposition of NiB and Cu on catalyzed PI film

In our previous study, a conductive seed layer of Cu was successfully deposited on a Pd-immobilized PI film surface by the electroless method.\(^ {10}\) In this study, an acceleration process was used – since the reactivity of the electroless Cu solution is low, an acceleration process is necessary to initiate electroless Cu deposition. In the acceleration process, the Pd-immobilized PI film was immersed in a solution containing dimethylamine borane (DMAB); then, the film was immersed in the electroless Cu plating solution without removing the residue of DMAB solution from the surface of the PI film (the residue was necessary to initiate electroless Cu deposition).

![Fig. 3 XPS spectra of the Si(2p) region of a layer of the organic molecules formed on the PI film surface. a) is with plasma pretreatment, b) is without plasma pretreatment.](image1)

![Fig. 4 XPS spectra of the Pd(3d) region of a Pd catalyzed layer; a) is with organic layer, b) is without organic layer.](image2)

![Fig. 5 Cross-sectional TEM image of a specimen consisting of island-like NiB and electroless Cu deposits.](image3)
The acceleration process caused deterioration of the electroless deposition solution and also a decrease in peel strength of the obtained films. Therefore, a different method to form electroless NiB deposits before electroless Cu deposition was introduced. Electroless NiB was deposited on the Pd-immobilized PI film surface without performing the acceleration, because the reactivity of the electroless NiB solution containing DMAB as the reducing agent is higher than that of the electroless Cu solution. The deposition time used in this study for NiB was 15 sec or 60 sec. (The deposition rate of NiB was 1.2 µm hr⁻¹.) When the deposition time was 15 sec, the deposit consisted of discontinuously distributed islands of NiB. On the other hand, when the deposition time was 60 sec, the deposit formed a continuous layer of NiB.

Electroless Cu plating as a seed layer was performed for 60 sec on the both electroless NiB underlayers (the plating time of electroless NiB was 15 sec and 60 sec). The deposition of electroless Cu as a conductive layer on the PI film became possible with an electroless NiB underlayer. Figure 5 shows a cross-sectional TEM image of the specimens consisting of discontinuous NiB and electroless Cu deposits. It was confirmed that the interface between the plated film and the PI film was very smooth. Based on all the observations that were made, this process is adaptable to the fabrication of circuits for use at high frequencies of electric signals.

3. 3 Peel strength measurement of electrodeposited Cu film

A 10 µm thick layer of Cu was electrodeposited on the PI film modified with conductive seed layer. The specimens were line-patterned by the subtractive method. The patterned specimens were used for the 90° peel strength test. Figure 6 shows the variation of peel strength with annealing time. The specimens consisted of the PI film substrate, the discontinuous (Fig. 6-a) and the continuous (Figs. 6-b and 6-c) NiB underlayer, electroless Cu deposit 30 nm in thickness, and the electroplated Cu 10 µm in thickness. Figures 6-a and 6-b show the values of peel strength of the lined patterns with the width of 0.1 mm, while Fig. 6-c shows the value of peel strength of the lined pattern of 1 mm in width. Figure 6-a shows that the peel strength of the specimens with discontinuous NiB underlayer (plating time was 15 sec) rapidly decreased during annealing at 150°C. The averaged peel strength before annealing was 0.26 kN m⁻¹, which decreased to 0.05 kN m⁻¹ after 48 hrs of annealing, and, in some cases, the Cu film peeled off the substrate at longer annealing times. The rapid decrease in peel strength of these specimens may have been caused by the direct contact of Cu to the APTES layer, which happened because the NiB underlayer was discontinuous. In the following results, in the case of electroless NiB underlayer was continuous, the adhesion strength was not decreased by annealing. It was reported in References 16, 17, and 18 by Furman et al., Miura et al., and Maeda et al. that this direct contact causes the delamination of the PI film at the interface, 16,17 and that the Cu wire is corroded by a minute amount of water remaining on the surface of the PI film.18 It is clear that the APTES layer may not function as a barrier layer preventing Cu from contacting the surface of the PI film.

Figure 6-b shows that, initially, the peel strength increases with annealing time; after a maximum increase about 24 hrs of annealing time, it first decrease rapidly and then gradually. As is clear in Figs. 6-a and 6-b, use of a continuous NiB underlayer improved the adhesion strength. The deposition of a continuous layer of NiB is essential to prevent the degradation of adhesion strength that occurs during annealing at 150°C.

Figure 6-c shows the value of peel strength of a specimen with the line width of 1 mm. The peel strength of the specimen was higher than the peel strength for the specimens with line width of 0.1 mm. The peel strength is expected to be independent of the width of line pattern, as it is a value normalized in the calculation with respect to line width. The difference in peel strength that were observed between different line widths may be attributable to the difference in the extent of overetching. The interface between the Cu and PI film underneath the lined pattern was exposed to the etching solution in the last stage of the subtractive process, and the side etching might have both the electroless NiB underlayer and the electroless Cu conductive layer. The etching solution damages the interface. Since this damage is relative to the line width, it might be more pronounced for narrower line than for wider ones. This may be one reason for the difference in peel strength between different line widths.

The peel strength of the specimens with continuous NiB underlayer did not decrease in the early stages of annealing. It was considered that the continuous layer of NiB serves as a barrier that prevents direct contact of Cu with the PI surface modified with APTES.
3.4 Investigation of the origin of electrodeposited Cu film delamination

To find out the location at which the delamination occurred, the surfaces of both the Cu and the PI film after delamination were investigated by XPS.

The specimens used in this experiment consisted of a PI film substrate, a discontinuous NiB underlayer, electroless Cu seed layer, and electrodeposition Cu layers, and they were not annealed. Figure 7 shows the XPS spectra of the delaminated surface of the PI film (Fig. 7-a) and of the Cu film (Fig. 7-b). For the delaminated surface of the PI film, we observed a pronounced peak for nitrogen N(1s), which mainly originated from the imide bond of the film itself and not from the APTES layer. For the delaminated surface of the Cu layer, we did not observe any peak for N(1s). These different observations could be the result of the fact that PI film includes a large number N groups, whereas APTES contains only a few N groups. For the delaminated surfaces of both the PI film and the Cu layer, we observed pronounced peaks for silicon Si(2p). This similar observation indicates that the silicon originated from the APTES layer–it is assumed, therefore, that delamination occurred within the APTES layer.

An interesting result was obtained from the annealed specimens, which were delaminated after annealing at 96 hrs. Figure 8 shows the XPS spectra of the delaminated surfaces of the PI film (Fig. 8-a) and of the Cu layer (Fig. 8-b). For the delaminated surfaces of both the PI film and the Cu layer, we observed pronounced peaks for nitrogen N(1s), which originated from the imide bond of the PI film. It was expected that there would be pronounced peaks from the APTES layer for silicon Si(2p), but none was observed. These XPS results suggested that the delamination occurred from the PI film. In the case of the Cu directly in contact with the PI film, the Cu atoms and the carboxyl group of the PI film must have reacted with each other during annealing. The layer of vulnerability was formed in the PI film by annealing. Therefore, the peel strength might be decreased by annealing, and the delamination occurred from the PI film. On the other hand, in the case of the specimens with a continuous NiB underlayer, the delamination is assumed to have taken place within the APTES.

![Fig. 7 XPS spectra of the delaminated surfaces of the specimens before annealing. The specimen consisted of a discontinuous NiB underlayer, an electroless Cu layer 30 nm in thickness, and an electrodeposited Cu layer 10 μm in thickness. Spectra (a) and (b) were obtained from the delaminated surfaces of PI and Cu film, respectively.](image1)

![Fig. 8 XPS spectra of delaminated surfaces of the specimens after annealing at 96 hrs. The specimen consisted of a discontinuous NiB underlayer, an electroless Cu layer 30 nm in thickness, and an electrodeposited Cu layer 10 μm in thickness. Spectra (a) and (b) were obtained from the delaminated surfaces of PI and Cu film, respectively.](image2)
layer either before or after annealing.

The presence of the APTES layer is essential for bond to the deposited layer strongly to the surface of PI film.

4 Conclusions

The use of electrochemical methods to form a Cu layer on the PI film was investigated. Generation of the OH groups on the surface of the PI film was confirmed by contact angle measurement and FT-IR, and formation of the APTES layer was confirmed by XPS. Plasma irradiation is an essential treatment for the formation of an APTES layer onto the PI film.

The surface smoothness of the PI film remained unchanged after each step. By use of APTES as a catalyst immobilizing layer, an electroless plated metal film was successfully fabricated on the surface of the PI film. The smooth interface between the plated film and the PI film was confirmed by TEM. Therefore, this process is suitable for the fabrication of circuits to be used at high frequencies of electric signals.

Cu wiring was successfully fabricated by a subtractive process, and a pull test was performed to measure the adhesion property. It was found that the use of the combination of a NiB underlayer and a Cu seed layer, both deposited by electroless methods, improved the adhesion strength of the Cu wire. It was found that use of a continuous NiB underlayer improved the adhesion strength. The deposition of a continuous layer of NiB is essential to prevent the degradation of the adhesion strength that occurs during annealing at 150 °C. When the continuous NiB underlayer was used, delamination occurred within the APTES layer. The target value of peel strength is 0.5 kN m⁻¹ when the line width and the film thickness are 0.1 mm and 10 μm, respectively. The results obtained in this experiment are inferior but close to the target value.

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