Direct Electroless Silver Plating on Copper Metal from Succinimide Complex Bath Using Imidazole as the Reducing Agent

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Direct electroless silver plating on copper metal from a succinimide complex bath using imidazole as the reducing agent was examined. Though the electroless silver plating from this bath is essentially an autocatalytic deposition, there is a problem in the properties and adhesion of the plated film because of the substitution deposition of silver due to the dissolution of the base copper metal that occurs during the first stage of plating. By adding glyoxylic acid, which is catalytically reacted on the copper surface to emit electrons, as the second reducing agent, the substitution deposition of silver was suppressed, the surface condition became dense and the adhesion was improved. It has been determined that the mixed potential theory can be applied to this reaction based on the result of the local polarization curve measurement.

Key Words: Electroless Silver Plating, Cyanide Free, Copper Substrate, Deposition Mechanism

1. Introduction

Silver has the lowest specific resistance, it is comparatively cheap, and excels in soldering among the various metal elements, therefore, it is widely used as a surface treatment material for general-purpose contact points and various electronic parts. In particular, as miniaturization of electronic parts occurs, it is difficult to apply a plating of uniform thickness for minute parts having a complex shape by electroplating, which has a problem with the current distribution uniformity. Consequently, silver plating by electroless deposition is demanded as a new functional material in fields related not only to contact parts but also to optics and semiconductors.

Recently, the adoption of BGA (Ball Grid Array) type electronic parts and the buildup substrate, which can be wired in high density, has increased for use in electronic equipment in which miniaturization and weight-saving are rapidly proceeding. However, the buildup substrate tends to increase the cost though possible to be wired in a high density compared with a conventional IVH (Interstitial Via Hole) substrate. Moreover, though electroless nickel-phosphorus/gold plating has been conventionally adopted for the copper pad of the printed wiring substrate to secure the reliability of the contact point in the shielding case, the nickel diffuses to the surface of the gold plating through pinholes, etc., in the gold plating layer, and the soldering quality deteriorates due to the formation of nickel oxide and hydroxide, which causes a decrease in the strength of the solder bonding part. The adoption of silver plating for the printed wiring substrate can solve these problems. Currently, silver plating has been practically applied to the main substrate of some models of cellular phones though it is a displacement plating type reaction. It is considered that its use will expand further if the silver plating by the autocatalytic deposition becomes possible in which a predetermined thickness plating can be obtained directly on the copper base metal.

We have already reported that the electroless silver plating bath using an organic nitrogen compound as the complexing agent and reducing agent excels in stability and the silver film is autocatalytically deposited. In this report, the possibility of electroless silver plating on copper base metal using this bath was examined, and the application of glyoxylic acid as the second reducing agent was examined in order to suppress the substitution deposition of silver due to the dissolution of the copper base metal.

2. Experimental

2.1 Film thickness, deposition rate, and film appearance

The basic bath composition and the plating conditions are listed in Table 1. Rolled sheet copper (4 cm²), which was alkaline electrolytically degreased, was used as the main substrate. The AgNO₃ concentration was fixed at 0.012 mol/L, the succinimide concentration at 0.020 mol/L, and the concentration of hydrazine at 0.020 mol/L. The pH was maintained at 7.0. The temperature of the electroless silver plating bath was 50°C. The film thickness of the silver plating was determined to be 0.5-1.0 μm.

Table 1 Basic bath composition and plating condition of electroless silver plating.

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
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<tbody>
<tr>
<td>AgNO₃</td>
<td>0.012 mol/L</td>
</tr>
<tr>
<td>Succinimide</td>
<td>0.020 mol/L</td>
</tr>
<tr>
<td>Imidazole</td>
<td>0.020 mol/L</td>
</tr>
<tr>
<td>pH</td>
<td>7.0</td>
</tr>
<tr>
<td>Bath temperature</td>
<td>50°C</td>
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becomes equal'. In this study, a local polarization curve reducing agent and the reduction rate of the metal ion a mixed potential (Emp) where the oxidizing rate of the metal ion based on the mixed potential theory. The mixed potential theory suggests that the plating reaction proceeds at the electrode interface though it is mixed potential, that the copper ion is oxidized to 2 valence due to the substitution reaction, has a large possibility to be a film with poor adhesion which causes easy peeling at the interface with the substrate, it is necessary to suppress the substitution deposition as much as possible. In this study, glyoxylic acid, which is catalytically reacted on copper surface to emit electron $e^-$, was added to the basic plating bath as the second reducing agent, and the effect was examined. Glyoxylic acids of predetermined concentrations were individually added to the basic plating bath indicated in Table 1. After soaking the copper base metal in each plating bath for a predetermined period, the copper ion concentrations in the plating bath were determined using the RF plasma emission spectrophotometer (SPS-7700 made by Seiko Instruments Inc.; hereafter abbreviated ICP). The solution, which excluded silver nitrate from the basic plating bath composition indicated in Table 1, was used for the measurement of the local anodic polarization curve. Moreover, the local anodic polarization curve in each single solution of imidazole, succinimide, and the glyoxylic acid was measured. In the measurement of the local cathodic polarization curve, the solution that excluded imidazole from the basic plating bath composition was examined. Nitrogen gas was aerated through the solution for 20 minutes before the measurements, and oxygen dissolved in the solution was eliminated.

3. Results and discussion

3.1 Film thickness, deposition rate, and amount of dissolved copper by electroless silver plating on copper metal

Figure 1 shows the relation between the plating time, the thickness of the obtained silver coating and the amount of dissolved copper. The film thickness of the silver coating increased as the plating time increased. On the other hand, the amount of copper dissolved in the plating bath by the substitution reaction linearly increased for three hours after the start of plating, and then reached almost a constant value. As a result, it is measured by the potentiodynamic method to clarify the deposition mechanism of this electroless silver plating and to confirm whether or not the mixed potential theory is applicable to this process. The HZ-3000 electrochemical system (made by Hokuto Denko Corporation) was used for the measurements at the potential scanning rate of 10 mV/s. A silver-plated platinum disc of 2 mm in diameter, embedded in a Teflon folder, was used as the working electrode, and the silver plating of about 3 μm in thickness was done at a cathodic current density of 10 mA/cm² before each measurement. A platinum wire was used for the counter electrode and the silver-silver chloride electrode (KCl 3.3 mol/L) was used for the reference electrode. The electrode potentials in this study are values based on this reference electrode.

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considered that the silver deposition in this bath is based on the autocatalytic reaction.

The deposition rates when the various factors were individually changed under the condition of the plating and the basic plating bath composition indicated in Table 1 are shown in Figure 2. The deposition rate of silver increased as the concentration of silver nitrate, the concentration of imidazole, and the bath temperature increased. Moreover, it decreased as the concentration of succinimide increased. The deposition rate of silver increased as the concentration of imidazole increased, and a continuous deposition was not observed in the bath which did not contain imidazole. Consequently, it is considered that imidazole worked as a reducing agent. The effect of pH on the deposition rate was remarkable, and the deposition rate decreased as the pH increased. Moreover, an increase in the deposition rate due to an increase in the bath temperature was observed. Based on these results, a neutral plating condition and low temperature can be used for the electroless silver-plating bath when succinimide is the complexing agent, imidazole is the reducing agent, and the bath composition and the plating conditions shown in Table 1 are considered to be optimum.

3. 2 Effect of concentration of glyoxylic acid on amount of dissolved copper and film thickness

Glyoxylic acid of 0.010 mol/L, 0.030 mol/L, and 0.050 mol/L were individually added to the basic plating bath indicated in Table 1, and the copper base metal was soaked in each plating bath for a predetermined period. The result of examining the effect of the concentration of glyoxylic acid on the amount of deposited silver and dissolved copper is shown in Figures 3 and 4.

In Figure 3, the effect of the concentration of glyoxylic acid on the thickness of the obtained silver film is shown, and the thickness of the silver film obtained from the basic plating bath shown in Table 1 is indicated by the symbol “○”. It is understood that the thickness of the deposited silver film decreased as the concentration of glyoxylic acid, which was added in the basic plating bath, increased.

Figure 4 shows the effect of the concentration of glyoxylic acid on the amount of copper, which was dissolved in the plating bath by the substitution reaction, the amount of copper dissolved from the base metal decreased as the concentration of glyoxylic acid increased. Moreover, the substitution reaction with copper almost stopped in about three hours after starting the plating in the basic bath without glyoxylic acid addition. On the other hand, the substitution reaction stopped in about
two hours after starting the plating for the 0.010 mol/L glyoxylic acid added bath, and in about one hour after starting the plating for the 0.030 mol/L and 0.050 mol/L glyoxylic acid added baths.

Figure 4 shows the amount of copper dissolved in the basic plating bath and the glyoxylic acid-added bath by the substitution reaction with silver. Figure 5 shows the amount of silver deposited by the autocatalytic reaction, where the amount of silver due to the substitution deposition is calculated from this amount of dissolved copper measured by the ICP method; this amount is subtracted from the total amount of deposited silver. From this figure, it is understood that the silver deposition by the substitution reaction was suppressed as the concentration of the glyoxylic acid increased. Based on this result, the decrease in the total amount of the silver deposition (Figure 3) obtained from the baths can be understood: basic plating bath, 0.010 mol/L glyoxylic acid-added bath, 0.030 mol/L glyoxylic acid-added bath, and 0.050 mol/L glyoxylic acid-added bath, is attributed to the decrease in the amount of the substitution deposition.

Such an action of the glyoxylic acid is schematically expressed in Figure 6. In the bath without glyoxylic acid, the silver particle is deposited on the base metal by the substitution reaction of copper with the silver ion. It is considered that the deposited silver particles behave as the nucleus during the electroless plating reaction, nuclear growth on the surface occurs rather than new nucleation on the base metal, therefore, the particle size increases, and more time is required to mask the base metal. On the other hand, in the glyoxylic acid-added bath, the nucleation by the oxidation reaction of the glyoxylic acid on the copper base metal simultaneously occurs with the nucleation due to the substitution reaction as shown in Figure 6. However, it is considered that generation of the silver nucleus caused by the glyoxylic acid occurs rather than nuclear growth of the generated silver nucleus, therefore, the particle size is small, and the masking of the base metal is completed in a short time. The addition of the glyoxylic acid into the basic plating bath causes the decrease in the rate of autocatalytic silver deposition, which can be due to the decrease in concentration of liberated imidazol formed through the azomethyne-forming condensation of the imide group with the aldehyde group of the glyoxylic acid.

Moreover, it was confirmed that the electroless copper deposition, which used the glyoxylic acid as a reducing agent, from the copper ion dissolved into the bath by the substitution reaction did not occur in the neutral range. From these results, it was understood that the glyoxylic acid added as the second reducing agent was effective in suppressing the substitution deposition of silver.

3. 3 Appearance of electroless silver plating film on copper metal

Figure 7 shows the SEM images that describes the effect on the initial deposition of silver by adding glyoxylic acid, which was added to the basic plating bath as the second reducing agent in order to suppress the substitution deposition of silver. Both are surface conditions of the silver plating having a film thickness of about 0.5 μm. In the silver plating film obtained from the basic plating bath, which did not include glyoxylic acid, the silver particles, which were deposited during the initial deposition stage, were comparatively large. On the other hand, the deposited silver particles in the film obtained from the glyoxylic acid-added bath
became small while increasing the concentration of the glyoxylic acid. This is considered to be the reason why it did not require time to mask the base metal and suppress the substitution deposition reaction. Moreover, the deposited silver film did not peel off during the tape peeling off testing, which indicated excellent adhesion.

3.4 Deposition mechanism

Concerning the deposition mechanism of the electroless silver plating in which succinimide was used as the complexing agent and imidazole was used as the reducing agent, we have already clarified it in a previous report. In this study, the effect when glyoxylic acid was used as the second reducing agent exerted on the deposition behavior of silver was examined by polarization measurements using potentiodynamism. The result is shown in Figure 8. The solution, which excluded silver nitrate, a metal salt, from the basic plating bath composition indicated in Table 1 was used for the measurement of the local anodic polarization curve. Moreover, the anodic polarization curves of this solution to which 0.010 mol/L glyoxylic acid was added, and the 0.010 mol/L glyoxylic acid single solution (pH=7 for both solution) were also measured. In the measurement of the local cathodic polarization curve, the solution, which excluded imidazole from the basic plating bath composition shown in Table 1, was examined. Curve "e" is the anodic polarization curve of the glyoxylic acid single solution, and the anodic current flowed in the potential range nobler than about –0.2 V. Moreover, an anodic
current flowed from about $-0.2$ V in the anodic polarization curve “f” for the solution which contained 0.010 mol/L glyoxylic acid in the basic plating bath. However, because the anodic current at about 0.22 V where the mixed potential exists, is almost equal to the local anodic polarization curve “a” obtained from the basic plating bath, it is considered that the anodic current around $-0.2$ V of curve “c” is attributed to the oxidation reaction of the glyoxylic acid, and the anodic current around 0–0.6 V is mainly attributed to the oxidation reaction of imidazole. Based on the results of Figure 5 and Figure 8, it is elucidated that the effect of the glyoxylic acid, which is the second reducing agent, on the deposition behavior of silver is negligible. The natural electrode potential of the silver electrode in the basic plating bath to which 0.010 mol/L glyoxylic acid had been added was 0.24 V, and it almost coincided with the mixed potential obtained from local polarization curves “c” and “d” in Figure 8. Moreover, the calculated value of the silver deposition rate obtained from the current value in this mixed potential almost coincided with actual data of the silver deposition rate obtained from this bath. Consequently, it has been determined that the mixed potential theory is applicable to this reaction.

4. Conclusion

Concerning the electroless silver plating from a neutral bath which uses an organic nitrogen compound as the complexing agent and reducing agent, the plating conditions to deposit the silver coating during autocatalytic deposition have been established. The possibility of using a second reducing agent to suppress the substitution deposition of silver due to the dissolution of the copper basis metal was examined. The deposition behavior of silver was electrochemically analyzed by measuring the local anodic polarization and local cathodic polarization. As a consequence of this study, the following results were obtained.

1) The electroless silver plating bath containing succinimide, which is an organic nitrogen compound, as a complexing agent, and imidazole as a reducing agent, exhibited the features that it could be used under neutral and low temperature conditions considering the durability of the organic resist, and it does not contain cyanide. The silver film was deposited by an autocatalytic reaction from the bath, and the bath also excelled in stability. Moreover, neither the turbidity of the plating bath nor the abnormal deposition of silver was observed.

2) The silver deposition by the substitution reaction with copper could be suppressed by adding glyoxylic acid as the second reducing agent. Moreover, the silver film, which was obtained from the glyoxylic acid-added bath, exhibited a dense and smooth surface with excellent adhesion because the particle size of the deposited silver decreased with an increase in the concentration of the glyoxylic acid.

3) The mixed potential obtained from the local anodic and cathodic polarization curve in the basic plating bath almost coincided with the natural electrode potential of the silver electrode in the plating bath. Moreover, the actual silver deposition rate coincided with the calculated value of the silver deposition rate obtained from the current value at the mixed potential. From these results, it has been determined that the mixed potential theory is applicable for the reaction in the electroless silver-plating bath used in this study.

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