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Gold wire bondability of electroless gold plating using disulfiteaurate complex

H. WATANABE, S. ABE

Graduate School, Kanto Gakuin University, 4834 Mutsuura-cho, Kanazawa-ku, Yokohama-shi, Kanagawa 236, Japan

H. HONMA

Faculty of Engineering, Kanto Gakuin University, 4834 Mutsuura-cho, Kanazawa-ku, Yokohama-shi, Kanagawa 236, Japan

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Generally, contact or terminal areas are coated with nickel as a barrier layer; subsequently, gold plating is performed to maintain reliability of electrical interconnection. Treatment using dilute solutions of palladium ions have been applied to initiate electroless nickel plating on copper substrates because copper has no catalytic action for the oxidation of hypophosphite. However, trace amounts of palladium ions may remain on the unwanted areas and extraneous nickel deposits are often observed. We confirmed that nickel films without extraneous deposits can be formed using the activation solutions containing dimethyl amine borane (DMAB). Bondability on the electrolessly deposited gold was greatly influenced by the phosphorus contents of the deposited nickel films as the underlayer. Bonding strength after electroless gold plating was increased with increasing phosphorus contents in the nickel films. Stabilizers in the electroless gold plating also influenced the bonding strength. Baths containing cupferron or potassium nickel cyanide as a stabilizer showed superior bondability. Gold deposits having strong orientation with Au(220) and Au(311) indicated high bond strength.

Keywords: *wire bondability*, *electroless gold plating*, *noncyanide bath*, *disulfiteaurate complex*, *electroless nickel plating*, *activating treatment*

1. Introduction

Recently, minaturization of LSI (large scale integrated circuits) and PCB (printed circuit boards) have become essential with the downsizing of electronic devices. Electrogold plating is applied to electric wiring or terminals for improvement of conductivity and corrosion resistance. However, electroplating is not applicable since the circuits are becoming finer and denser. Accordingly electroless gold plating is an indispensable technology for metallization of circuits. Generally, cyanide baths have been used extensively for electroless gold plating [1–4]. However, plating solution containing cyanide ions is toxic and penetrates into the photoresist easily. Currently, noncyanide electroless gold plating baths have attracted interest [5–14] since noncyanide baths are less toxic and do not penetrate the photoresist. The purpose of this work is the development of noncyanide electroless gold plating using disulfiteaurate as a metal source and the evaluation of the wire bondability of deposited gold films.

2. Experimental details

2.1. *Electroless gold plating process*

The pretreatment process is shown in Table 1. Generally, an activating treatment with a low concentration of palladium ions is applied before electroless nickel plating on copper substrates since copper has no catalytic action for initiation of nickel deposition [15]. However, palladium ions tend to adsorb at unwanted areas and lead to extraneous deposits. Therefore, selective activation treatment using dimethyl amine borane (DMAB) was applied.

2.2. *Plating bath compositions and operating conditions*

The composition and conditions for electroless nickel and gold plating baths are shown in Tables 2 and 3, respectively. Nickel sulfate as a metal source and hypophosphite as a reducing agent are used in electroless nickel plating. Bondability of electroless gold films is influenced by the phosphorus contents in electroless nickel films as a barrier layer. Accordingly, electroless nickel films with various phosphorus

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Table 1. Pretreatment process

Alkaline degreasing (40 °C, 5 min)
⇩
Rinsing (40 °C, 3 min)
⇩
Rinsing (r.t., 1 min)
⇩
10% H_2SO_4 (40 °C, 5 min)
⇩
Rinsing (r.t., 1 min)
⇩
0.05 M DMAB (r.t., 40 s)
⇩
Electroless Ni plating
⇩
Rinse., N_2 agitation, r.t., 1 min
⇩
Electroless Au plating

contents (high, medium and low phosphorus) were evaluated by changing the complexing agents and operating conditions.

2.3. *Evaluation methods*

The copper fine pin grid alley (PGA) substrate (line/space 100/100 μm) was used in this study. Deposited nickel and gold on PGA substrates were observed with scanning electron microscope (SEM) and energy dispersive X-ray microscopy (EDX). The gold and nickel film thickness was measured by X-ray fluorescence. The contents of phosphorus were measured by plasma emission spectroscopy. Gold wire of 25 μm diameter (purity 99.99%) was used for bonding strength measurement. The bonding strength was measured and the wire fracture mode was observed using a tension gauge. The conditions for wire bonding are shown in Table 4.

Table 2. Electroless nickel plating bath compositions and operating conditions

High contents of phosphorus type	
$NiSO_4 \cdot 6H_2O$	0.05 M
Lactic acid	0.15 M
$NaPH_2O_2 \cdot H_2O$	0.15 M
pH	4.5
Temperature	90 °C
Medium contents of phosphorus type	
$NiSO_4 \cdot 6H_2O$	0.05 M
DL-Malic acid	0.15 M
$NaPH_2O_2 \cdot H_2O$	0.30 M
$Na_2S_2O_3$	1 ppm
pH	4.5
Temperature	90 °C
Low contents of phosphorus type	
$NiSO_4 \cdot 6H_2O$	0.05 M
Propionic acid	0.25 M
$NaPH_2O_2 \cdot H_2O$	0.15 M
pH	6.0
Temperature	50 °C

Table 3. Electroless gold plating bath composition and operating conditions

$Na_3[Au(SO_3)_2]$	0.006 M
Na_2SO_3	0.10 M
$Na_2S_2O_3$	0.10 M
NTA	0.10 M
L-Ascorbate	0.25 M
Stabilizer	10∼100 ppm
Agitation	Air
pH	6.0
Temperature	60 °C

3. Results and discussion

3.1. *Activation process for electroless nickel plating*

Generally, copper substrates have been treated with diluted palladium solution for initiation of electroless nickel plating. However, trace amounts of palladium ions tend to remain on the epoxy resin and many extraneous deposits on the epoxy resin were observed after electroless nickel plating as the underlayer. Accordingly, activation treatment of copper patterns with DMAB solution was evaluated in this study. Figure 1 shows SEM and EDX images of PGA substrate after electroless nickel plating. When copper patterns were activated with dilute palladium solution, epoxy substrate was covered with nickel after 3 min of plating. The entire surface was completely covered with nickel in 15 min (Fig. 1(A)). On the other hand, when copper patterns were activated using 0.05 M DMAB solution, the deposition reaction was completely suppressed on the epoxy substrate even after 15 min of plating (Fig. 1(B)). The adhesion strength between nickel and copper was superior and delamination between the copper and nickel interface did not occur using this activation method. From these results, selectivity differences of nickel deposition on the copper circuits by palladium and DMAB activation can be explained as shown in Fig. 2.

3.2. *Activation mechanism of copper activation by DMAB*

It was identified that electroless nickel plating started on the copper substrate using DMAB. Activation by DMAB can be explained as follows:

Table 4. Operating conditions for gold wire bonding

	First	*Second*
Ultrasonic power	75 mW	301 mW
Bonding force	55 g	90 g
Heat	120 °C	120 °C
Printed wire board temperature	100 °C	100 °C

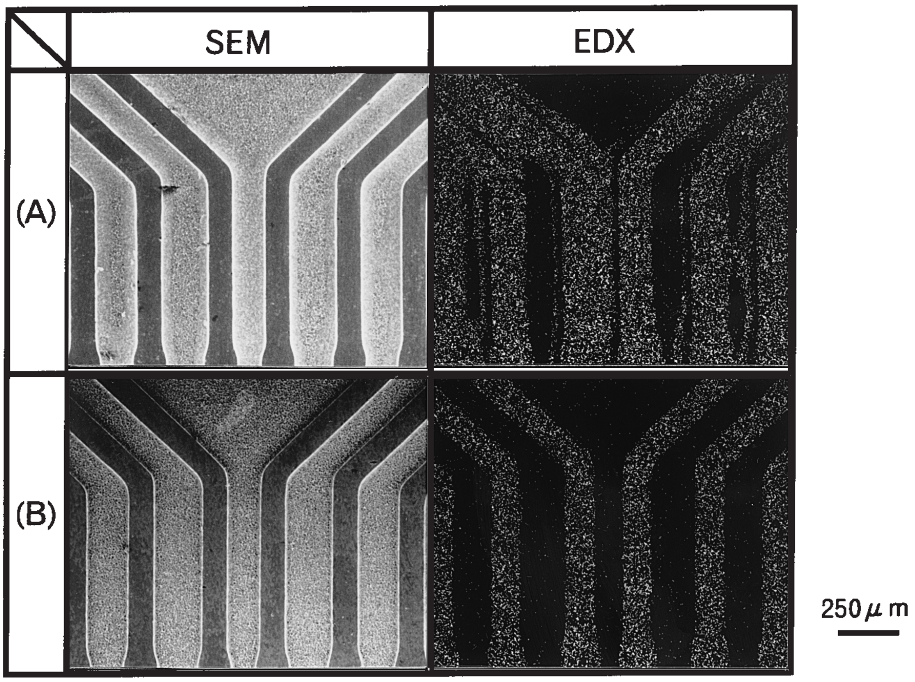

Fig. 1. SEM and EDX images of electroless nickel deposition on copper circuits initiated by palladium or DMAB activator: (A) activated by diluted palladium solution; (B) activated by DMAB solution.

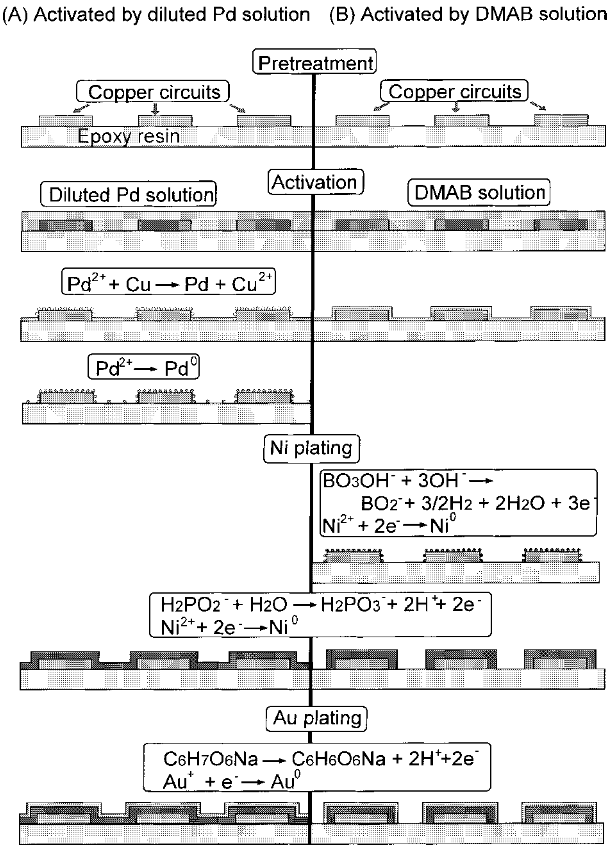

Fig. 2. Selectivity differences of electroless gold plating on copper circuits by palladium or DMAB solutions.

$$(CH_3)_2NHBH_3 + OH^- \longrightarrow (CH_3)_2NH + BH_3OH^-$$
$$+ BH_3OH^- + H_2O \longrightarrow BO_2^- + 3H_2 \qquad (1)$$

DMAB produces BH_3OH^- and electrons are discharged at the copper substrate by the anodic reaction [16, 17]. Subsequently, Ni^0 forms on the copper surface by the cathodic reaction:

$$BH_3OH^- + 3OH^- \longrightarrow BO_2^- + \tfrac{3}{2}H_2 + 2H_2O + 3e^- \qquad (2)$$

$$Ni^{2+} + 2e^- \longrightarrow Ni^0 \qquad (3)$$

Since the deposited nickel particles on the copper patterns have catalytic action for the oxidation reaction of hypophosphite, electroless nickel plating progresses autocatalytically.

3.3. *Operating conditions of activator*

Generally, the activating power of DMAB depends on the operating conditions of the activator (i.e. DMAB concentration, temperature, pH and dissolved oxygen concentration (DO) etc.). In this study, the temperature, pH and DO were selected as the variables of the activating conditions. The activating power of DMAB decreased with increasing temperature of the activating solution and spotty deposits were observed on the circuits above 60 °C. The efficiency as an activator gradually decreased due to the self-decomposition of DMAB at high temperature. Therefore, the activator must be maintained at room temperature.

The pH dependence of the activating power of DMAB was also examined. The electroless nickel plating reaction did not start below pH 7.0 and the copper patterns of PGA substrate were not fully covered with nickel at pH 8.0 to 9.0. Full coverage of nickel was found above pH 9.0. However, the pH of the activating solution decreased with reaction time and the activating power decreased, because DMAB itself has no buffer action. Therefore, boric acid was added to the activating solution as a buffer. The DO level in the solution also influences the activating power. The activating power increased with decreasing DO level in the activator by purging with nitrogen.

3.4. *Electroless gold plating and bondability*

The displacement reaction between nickel and gold takes place in the early stages of electroless gold plating. The displaced gold acts as the oxidation catalyst of the ascorbic acid and an auto catalytic reaction progresses as follows:

$$C_6H_8O_6 \longrightarrow C_6H_6O_6 + 2H^+ + 2e^- \quad \text{(on displaced gold)} \qquad (4)$$

$$[Au(SO_3)_2]^{3-} + e^- \longrightarrow Au + 2SO_3^{2-} \qquad (5)$$

The physical properties of gold also depend on the deposited nickel films. Accordingly, the following subjects related to the bondability were investigated: (i) phosphorus content in the electroless nickel films; (ii) effect of additives in the gold plating bath; and (iii) crystal orientation of gold films.

Approximately 5 μm of nickel was deposited on the copper patterns using high, medium or low phosphorus content type of nickel plating and 0.5 μm of gold was deposited using electroless gold plating. The bonding strength was measured by tension gauge. Approximately 100 measurement points were selected. The bonding strengths are shown in Fig. 3. Mean bonding values of 7.9 g were obtained with high phosphorus nickel and values of 6.4 g were obtained with medium phosphorus nickels. However, the bonding strength was below 1 g using low phosphorus nickel deposits. This suggested that the phosphorus content of the nickel films greatly influences the bondability.

3.5. *Influences of stabilizer on the bondability*

Electroless gold plating baths of noncyanide type were unstable and self-decomposition progressed after several hours. As reported previously [13], bath stability increases with addition of potassium ferrocyanide, cupferron, potassium nickel cyanide or 2,2′-bipyridyl as a stabilizer. In this study, the influences of the stabilizers on bondability were examined. As shown in Fig. 4, when a high phosphorus type of nickel as the under layer was applied, mean bonding values of 8.0 g were obtained. The highest bonding strengths were obtained with addition of cupferron or potassium nickel cyanide as stabilizer.

3.6. *Crystal orientation of deposited gold and bondability*

The relationship between crystal orientation of the deposited gold and bondability were investigated. The X-ray diffraction patterns of gold are shown in Fig. 5. Electroless gold films with high bonding strength were found to orient at Au(220), Au(311). Furthermore, X-ray diffraction patterns of deposited gold on nickel of high phosphorus type was also evaluated by the addition of stabilizers. The results are shown in Fig. 6. The gold film having strong orientation in Au(220), Au(311) demonstrated good bondability.

4. Conclusions

The bondability of electroless gold deposits using disulfiteaurate as a metal souce and the selectivity of nickel deposition as a barrier metal was investigated. The outcomes were as follows:

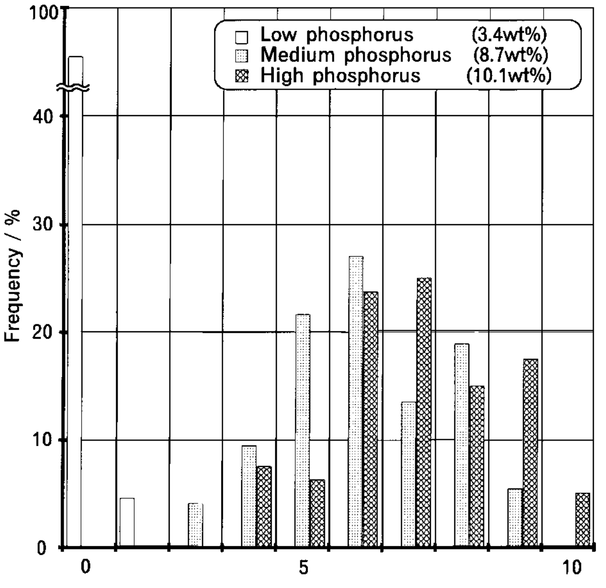

Fig. 3. Relationship between phosphorus contents of nickel film and adhesion strength of gold wire bonding.

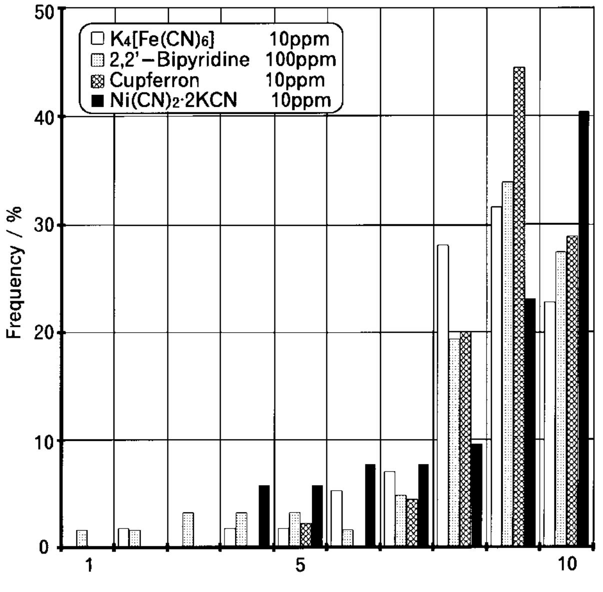

Fig. 4. Addition effects of stabilizer on adhesion strength of gold wire bonding.

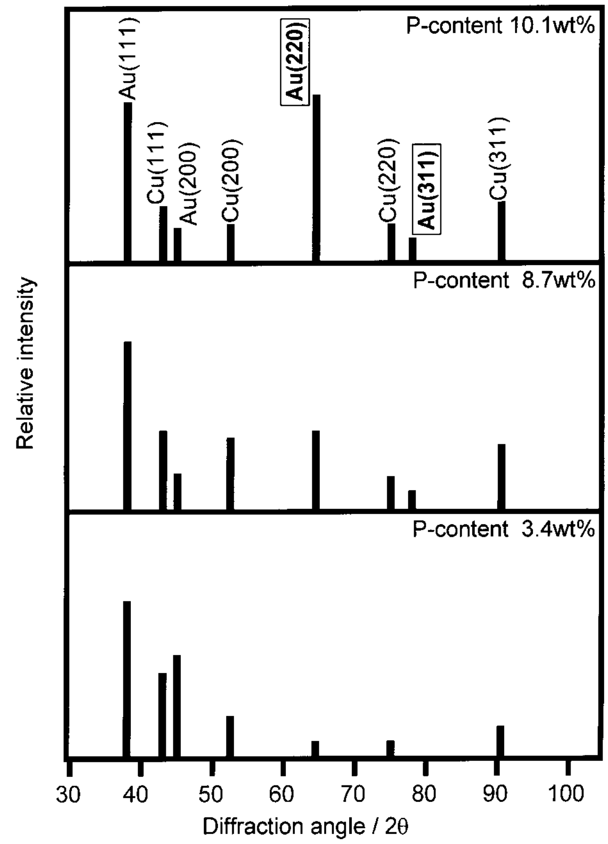

Fig. 5. X-ray diffraction patterns of electroless gold deposits.

(i) Selective electroless nickel films can be obtained on copper patterns of PGA substrate using DMAB solution instead of dilute palladium ion solution as activator. The activating power of DMAB solution depended on the operating conditions.

(ii) With increase in phosphorus content in the nickel films (around 10–12%), good bondability was obtained. Stabilizers for electroless gold plating also influenced the bonding strength. Baths containing cupferron or potassium nickel cyanide as a stabilizer showed high bondability.

(iii) Gold deposits having strong orientation with Au(220) and Au(311) showed good bondability.

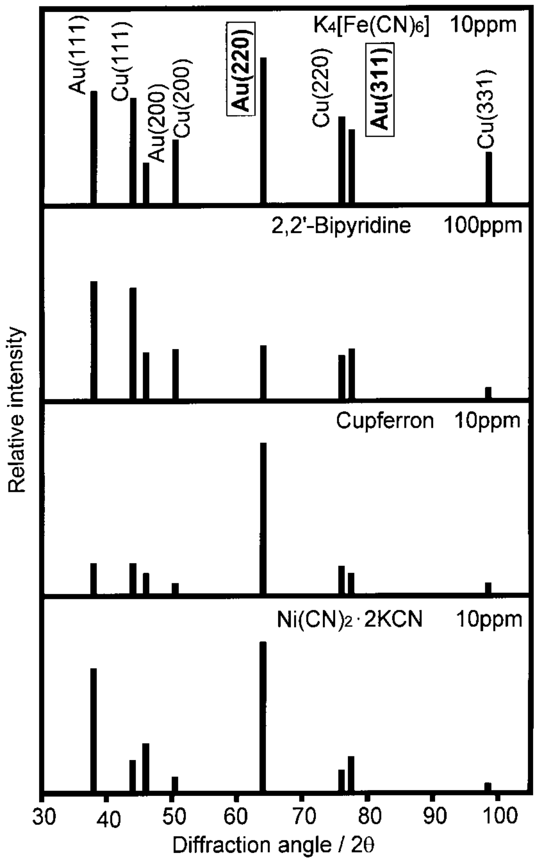

Fig. 6. Addition effects of stabilizer on crystal orientation of electroless gold film. (Electroless nickel film involved 10.1% of phosphorus.)

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