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Non-Cyanide Electroless Gold Plating Using Polyphenols as Reducing Agents

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Polyphenol compounds were investigated as reducing agents for non-cyanide electroless gold plating for electronics assembly applications. The pH value and temperature were optimized to determine the conditions that lead to a high deposition rate without precipitation. The surface morphology was evaluated by scanning electron microscopy. Catechol, pyrogallol, and gallic acid yielded deposited films with good appearance and solderability under the optimized conditions. Among the tested reducing agents, catechol is the most suitable for use as a stable plating bath with a long life. It has a moderate reducing ability to stabilize the bath and deposit the film. The calculated values of the heat of formation and the highest occupied molecular orbital levels of the reducing agents supported the experimental results.
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Gold has excellent electrical conductivity, chemical stability, heat stability, and ductility. Therefore, gold-plated films have been widely used for electronic applications such as printed circuit boards, connectors, wire bonding pads, solder ball pads, and bump electrodes. Among these applications, the market for ball grid alley (BGA) fabricated using organic circuit boards is growing.

Electrical conductive leads for electroplating in a BGA lead to signal delay and noise; these are obstacles that prevent high-density wiring.[1] When electroless plating is used to design the circuit the leads can be eliminated, thereby decreasing the delay and the noise.[2] Thus, high-density wiring can be realized. In addition, because of the capability of the technique of electroless plating to deposit gold selectively only in desired areas, this technique should be more economical to run than electroplating as far as the cost of gold is concerned.

Gold plating baths using cyanide compounds are stable and cost effective. Cyanide, however, is toxic and can lead to breakage in a photoresist. Therefore, sulfite and thiosulfate baths have been investigated. Inoue et al. developed electroless gold plating by using sulfite and thiosulfate salts as complexing agents and thiourea as a reducing agent.[3-5] Excess thiosulfite (intermediate gold–thiosulfate compound) leads to the codeposition of sulfur, and this makes the deposited gold harder.[6,7]

With regard to gold plating for BGA packages with a wire bonding pad and solder jointing, thick gold plating is advantageous for wire bonding; however, this leads to the generation of a brittle Au–Sn metal compound and the deterioration of solderability when solder balls are mounted on the pads. Therefore, the deposition of thin gold film is sufficient to mount solder balls. It was reported that the optimum gold thickness is 0.2 μm.[8] The deposition of a 0.2-μm-thick gold film by plating with the galvanic displacement reaction (often called the immersion process) is accompanied by the dissolution of the Ni substrate. Consequently, the solderability deteriorates. A stable process for gold deposition without dissolution reaction is required to deposit a gold film with a uniform thickness of 0.2 μm.

Ascorbic acid,[1,9-14] thiourea,[3-5] L-cysteine,[15] and hydroxyl amine[16] have been examined as reducing agents for electroless gold plating. However, ascorbic acid decomposes quickly, and sulfur compounds such as thiourea compete with other complexing agents such as ethylenediaminetetraacetic acid (EDTA) 2Na because of their own complexation capability. Iacovangelo and Zarnoch developed a new technique of electroless gold, termed substrate-catalyzed electroless plating, with hydrazine and dimethylamine borane in a cyanide bath.[17,18] Kato et al. applied this technique for a non-cyanide process.[19,20]

We aimed to develop a stable near-neutral, non-cyanide electroless gold plating process without the dissolution reaction of the substrate. Inoue et al. also adopted hydroquinone (1,4-benzendiol) as a scavenger for reducing the oxidized thiourea.[3-5] However, we selected polyphenol compounds as the reducing agents. They neither exhibit complexation onto gold nor disturb the activity of complexing agents.

Experimental

Bath composition.— The bath compositions and operating conditions are shown in Table I. Sodium gold sulfite was used as a gold source and phosphate salt was employed as a pH buffer. EDTA 2Na was used as a complexing agent. Catechol, pyrogallol, and gallic acid were tested as the reducing agents. These compounds have conjugated OH groups, which are oxidized easily.[21-23] The structural formulas of these reducing agents are shown in Fig. 1.

Specimen.— Copper plates were used as the specimens. Their size was 16 cm^2 (2 × 4 cm on both sides). Figure 2 shows the schematic diagram of the plating process. As a pretreatment, the specimens were degreased in an acid cleaner (EEJA EETOREX 15) and activated in 10% sulfuric acid. They were etched in a mixed solution of ammonium persulfate (100 g/L) and 10% sulfuric acid, and then they were dipped again in the 10% sulfuric acid. In order to activate the specimens for the subsequent electroless nickel plating, they were immersed in 30 mg/L of palladium chloride and 30 mL/L of hydrochloric acid. This pretreatment was carried out at room temperature. Then electroless nickel plating (EEJA Microfab NP7000) was performed at 85°C for 15 min, and galvanic displace-

Table I. Bath composition and plating conditions.

Bath composition		
$Na_3Au(SO_3)_2$	0.01	M
EDTA 2Na ($C_{10}H_{14}N_2O_8Na_2 \cdot 2H_2O$)	0.3	M
KH_2PO_4	0.04	M
Reducing agent	0.1	M
Plating conditions		
pH	5.0, 7.0, 9.0	
Temperature (°C)	45, 55, 65, 75	
Plating time (min)	15	

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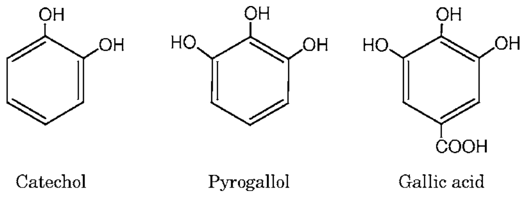


Figure 1. Structures of reducing agents.

ment gold plating (0.005 M $Na_3Au(SO_3)_2$, 0.2 M EDTA 2Na) was performed at 60°C for 10 min on the specimen prior to carrying out the gold plating usng the reducing agents.

Deposition rate and surface morphology.— The deposition rate was calculated by measuring the weight of the samples before and after the electroless gold plating for 15 min. The surface morphologies of the deposited films were observed with a scanning electron microscope (SEM: JEOL JSM-5410).

Solderability test.— The solderability of gold films from various baths was evaluated by measuring the zero cross time with a solder checker (RHESCA solder checker SAT-500). The zero cross time is defined as the time required for the meniscus to disappear, which is caused by the contact of a specimen with the molten solder. The solder temperature was 235°C; dipping time 5 s; and dipping rate 10 mm/s. The eutectic solder comprised 63% Pb and 37% Sn.

Stability test.— The deposition rate was monitored for 15 days to evaluate the life of the plating baths.

The stability of the plating baths was evaluated by monitoring the time variations of the deposition rate change with time.

Results and Discussion

Effects of the reducing agents on the deposition rate.— The deposition rate from the various reducing agent baths was calculated from weight gain. Figure 3 shows the dependency of the deposition rate on the plating temperature. Preliminary experiments revealed that the deposit thickness increased as a function of time on 10-μm-thick electrodeposited gold films for all the reducing agent bath, which suggested the autocatalytic mechanism. Each plot is the average of six data points. The deposition rate increased with the temperature and pH value.

All baths decomposed when the temperatures exceeded 75°C or when the pH exceeded 9.0; this is because a high pH accelerates the oxidation of the reducing agents. The reducing agents react only on the catalyzed gold at temperatures lower than 65°C, but the reaction occurs even in the bulk of the solution at temperatures higher than 75°C; the plating baths decomposed at 75°C.

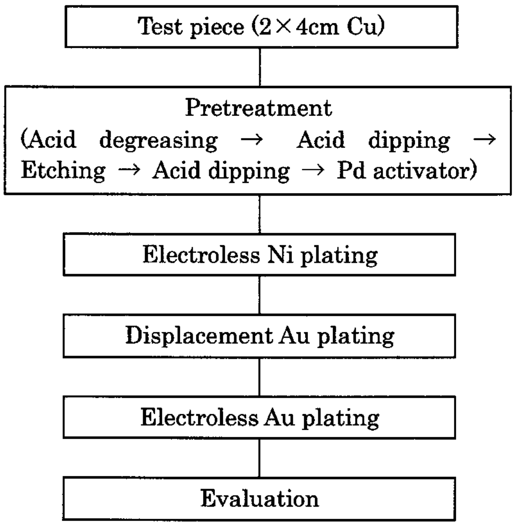


Figure 2. Schematic diagram of the plating process.

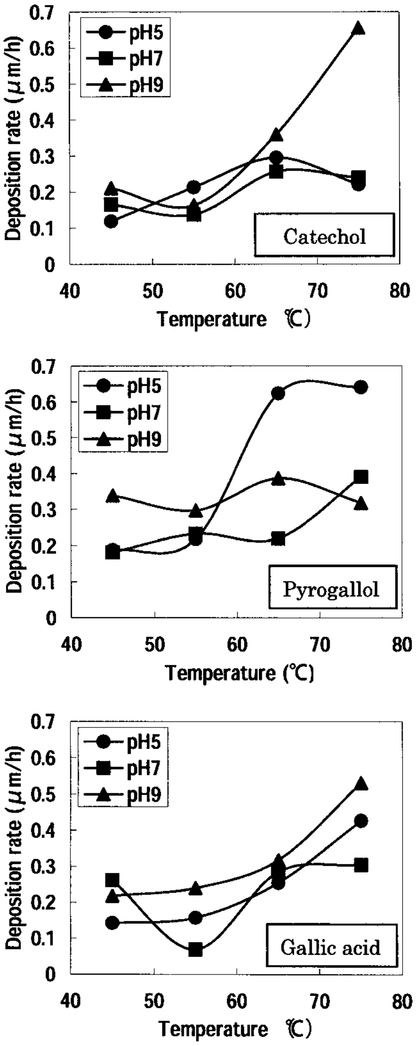


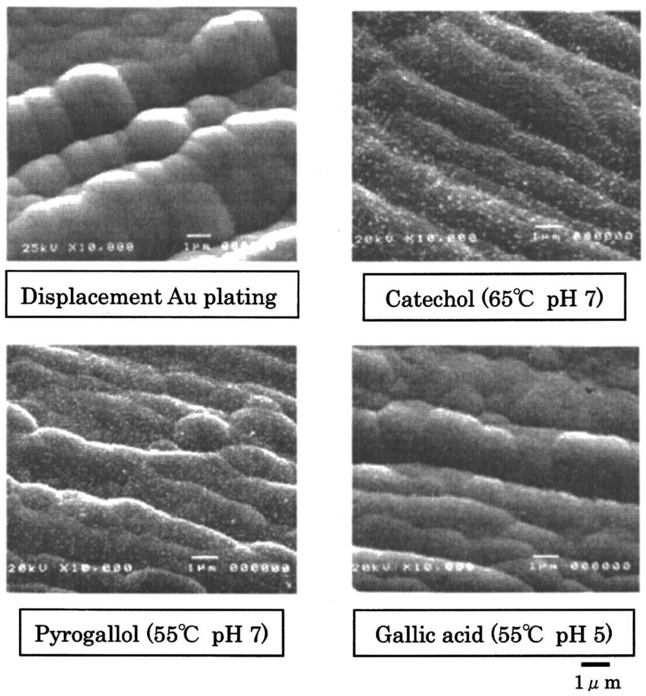
Figure 3. Effects of the reducing agents, pH values, and temperatures on the deposition rate.

The evaluation results of the appearances of the deposited surfaces are shown in Table II. In this table A, B, and C denote bright yellow, semibright yellow, and brown dendritic appearances, respectively. We investigated the optimum conditions for each bath—for the catechol bath, the optimum conditions were a temperature of 65°C and a pH of 7; for the pyrogallol bath, a temperature of 55°C and a pH of 7; and for the gallic bath, a temperature of 55°C and a pH of 5.

Table II. Appearance evaluation of deposited films.[a]

	Catechol			Pyrogallol			Gallic acid		
pH	5	7	9	5	7	9	5	7	9
45°C	B	A	B	A	A	A	A	B	A
55°C	B	A	A	B	A	A	A	A	B
65°C	B	A	A	C	A	B	A	C	C
75°C	A	A	B	C	A	A	B	B	B

[a] A = bright yellow, B = semibright yellow, C = brown dendritic.



Displacement Au plating

Catechol (65℃ pH 7)

Pyrogallol (55℃ pH 7)

Gallic acid (55℃ pH 5)

Figure 4. SEM images of the surface morphology for various reducing agent baths.

The deposited surface appeared to be coarse when the deposition rate exceeded 0.4 μm/h. When the gold concentration was not sufficient to compensate for the consumption of gold ions on the cathode interface (i.e., mass-transfer control), dense gold crystals did not grow, and the deposited film comprised dendritic crystals.

Surface morphology.— Figure 4 shows the SEM images of the deposited surface after the displacement gold plating and after the electroless plating under the optimum conditions. Gold grains with diameter of 10–100 were deposited uniformly in the case of the catechol and pyrogallol baths. As for the gallic acid bath, tabular grains were observed.

Solderability.— The solderability of the deposited films from the baths containing various reducing agents was evaluated. Figure 5 shows the test results using the wetting balance method (Meniscograph method). The zero cross time of all the films was less than 1 s, which is in accordance with the MIL spec for such films. This means that the deposited films obtained using the polyphenols exhibit the good solderability.

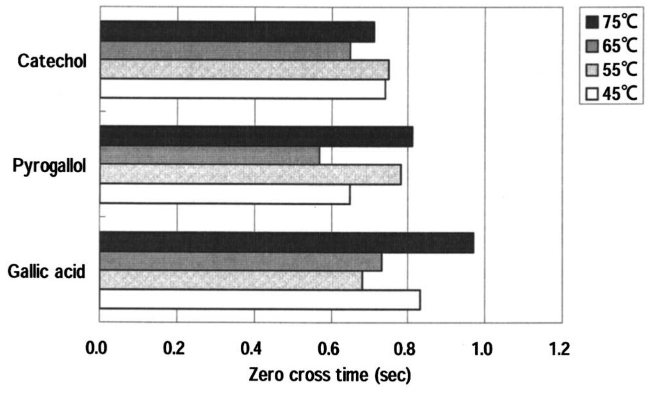


Figure 5. Zero cross time from the solderability test of the deposited films from the various reducing agent baths.

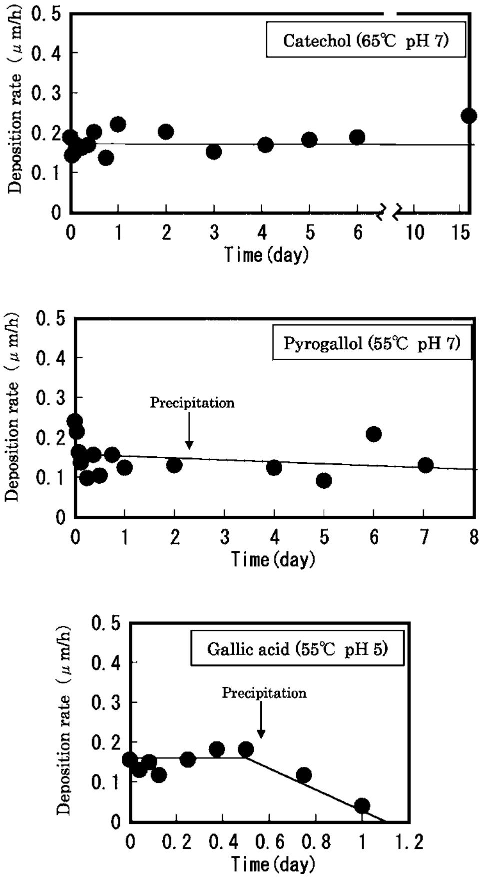
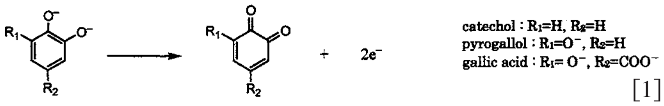


Figure 6. Time dependency of the deposition rate.

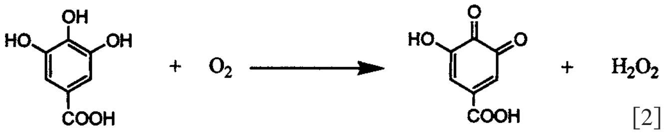
Stability.— The stability of the electroless plating baths was evaluated for the condition in which each bath leads to the best surface appearance and the highest deposition rate. The results for the catechol, pyrogallol, and gallic acid baths are shown in Fig. 6. No precipitation was observed in the catechol bath for 16 days after making the solution. The deposition rate was maintained constant during this period. Precipitation did not occur for 2 days in the pyrogallol bath and 15 h in the gallic acid bath. The deposition rate decreased in the gallic acid bath. From these results, it can be inferred that the electroless plating bath using catechol as the reducing agent was the most stable among the baths investigated in this study.

Although reducing agents with a strong reducing ability increase the deposition rate, the excessive reducing ability causes the decomposition of the plating bath. The reducing ability here is related to the oxidation potential. A reducing agent that has a strong reducing ability has a lower noble oxidation potential. Pyrogallol with three hydroxyl groups has a stronger reducing ability than catechol with two hydroxyl groups. In addition, gallic acid has an electron-withdrawing carboxyl group, and therefore, the reductant becomes more stable and the reducing ability increases. Gallic acid adsorbs onto metals and functions as a corrosion inhibitor;[24] this inhibits its performance as a reducing agent. This is consistent with the oxidation potentials measured by cyclic voltammetry. The order of the potentials in terms of decreasing nobleness was gallic acid > pyrogallol > catechol. This order signifies the reducing ability of the reducing agents. From the results of calculations by the PM3 method, the difference in heat of formation (ΔH_f) from the oxidation of the reducing agents (formula 1) were −30.0 kJ/mol for catechol, −269 kJ/mol for pyrogallol, and −362 kJ/mol for gallic acid



[1]

This order was consistent with the experimentally determined reducing ability. The highest occupied molecular orbital (HOMO) levels of the reducing agents were also calculated for catechol (+2.93 eV), pyrogallol (+8.15 eV), and gallic acid (+10.6 eV). These results were also in consistent with the reducing ability. Gallic acid reduces oxygen and its oxidation reaction is shown in formula 2[25]



[2]

Therefore, gallic acid is easily oxidized by dissolved oxygen; this decreases its activity. In this investigation, gallic acid and pyrogallol exhibited a very strong reducing ability, which induced the decomposition of the baths. Because of this excessively strong reducing ability, the reducing agents could be autoxidized and the gold ions were reduced not only on the substrate surface but also in the bulk of the solutions. In the case of catechol, a moderate deposition rate made the deposited film dense and smooth, which leads to better solderability.

Attempts to measure the reducing ability of the polyphenols by voltammetric experiments were unsuccessful. Due to the fact that voltammograms might be greatly affected by miscellaneous processes such as deprotonation of hydroxyl groups and changes in solvation that accompany the electrode process, we focused on the evaluation of the reducing ability by molecular orbital calculations.

Conclusions

We have investigated reducing agents having 1,2-hydroquinone moiety and concluded that gold plating baths containing these reducing agents are compatible for soldering applications in electronics assembly. The electroless plating bath containing catechol as the reducing agent exhibited the best performance among the reducing agents tested in this study. It had a life of 16 days and the deposition rate was constant during this period. The deposition rate increased with the temperature. When stability was taken into consideration, a temperature of 65°C was found to be the most suitable condition.

The stability of the catechol bath can be attributed to the moderate reducing ability of catechol, which is related to the heat of formation from the oxidation of the reducing agent and the HOMO level.

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References

1. K. Hasegawa, A. Takahashi, and A. Nakaso, *IEMT/IMC Proceedings*, p. 230 (1997).
2. P. E. Rogren, *Proceedings of the 15th IEEE/CHMT IEMT Symposium*, p. 485 (1993).
3. T. Inoue, S. Ando, H. Okudaira, J. Ushio, A. Tomizawa, H. Takehara, T. Shimazaki, H. Yamamoto, and H. Yokono, in *Proceedings of the 45th Electronic Components and Technology Conference*, p. 1059, IEEE (1995).
4. T. Inoue, S. Ando, J. Ushio H. Okudaira, H. Takehara, T. Ota, H. Yamamoto, and H. Yokono, *J. Surf. Finish. Soc. Jpn.*, **49**, 1298 (1998).
5. T. Inoue, *J. Surf. Finish. Soc. Jpn.*, **52**, 410 (2001).
6. T. Osaka, A. Kodera, T. Misato, T. Homma, Y. Okinaka, and O. Yoshioka, *J. Electrochem. Soc.*, **144**, 3462 (1997).
7. T. Osaka, M. Kato, J. Sato, K. Yoshizawa, T. Homma, Y. Okinaka, and O. Yoshioka, *J. Electrochem. Soc.*, **148**, C659 (2001).
8. A. Chinda, N. Miyamaoto, and O. Yoshioka, *J. Surf. Finish. Soc. Jpn.*, **49**, 1291 (1998).
9. M. Kato, K. Niikura, S. Hoshino, and I. Ohno, *J. Surf. Finish. Soc. Jpn.*, **42**, 729 (1991).
10. H. Honma, A. Hasegawa, S. Hotta, and K. Hagiwara, *Plat. Surf. Finish.*, **82**(4), 89 (1995).
11. M. Kato, Y. Yazawa, and Y. Okinaka, in *Proceedings of the 82nd AESF Technical Conference*, p. 805 (1995).
12. N. Hattori, K. Iwamatsu, K. Naito, K. Okuno, Y. Yazawa, K. Kuroiwa, and M. Kato, in *Proceedings of the 2001 ICEP*, p. 166 (2001).
13. S. Kawashima and H, Nakao, *IEMT/IMC Proceedings*, p. 226 (1997).
14. A. M. Sullivan and P. A. Kohl, *J. Electrochem. Soc.*, **142**, 2250 (1995).
15. T. Takeuchi, Y. Kohashi, D. H. Kim, H. Tanikubo, and S. Mizumoto, *Plat. Surf. Finish.*, **90**, 56 (2003).
16. J. Sato, M. Kato, K. Yoshizawa, H. Otani, T. Honma, Y. Okinaka, O. Yoshioka, and T. Osaka, in *Proceedings of the 101st Annual Conference of SFJ*, p. 246 (2000).
17. C. D. Iacovangelo and K. P. Zarnoch, *J. Electrochem. Soc.*, **138**, 976 (1991).
18. C. D. Iacovangelo, *J. Electrochem. Soc.*, **138**, 983 (1991).
19. M. Kato, J. Sato, H. Otani, T. Honma, Y. Okinaka, T. Osaka, and O. Yoshioka, *J. Electrochem. Soc.*, **149**, C164 (2002).
20. J. Sato, M. Kato, H. Otani, T. Honma, Y. Okinaka, T. Osaka, and O. Yoshioka, *J. Electrochem. Soc.*, **149**, C168 (2002).
21. P. Wu, S. Yasuda, H. Tachibana, and K. Yamada, Food Sci. Technol. Res., 9(2), 180 (2003).
22. K. Yamada, H. Tachibana, N. Matsuo, K. Nishiyama, and M. Sugano, Food Sci. Technol. Res., 5(1), 1 (1999).
23. Z. Cheng, J. Ren, Y. Li, W. Chang, and Z. Chen, Redox Rep., 7(6), 395 (2002).
24. Y. Shibata, T. Shiromoto, K. Tokoro, M. Yuasa, I. Sekine, T. Imahama, and T. Wake, *Denki Kagaku oyobi Kogyo Butsuri Kagaku*, **61**, 992 (1993).
25. V. Tulyathan, R. B. Boulton, and V. L. Singleton, *J. Agric. Food Chem.*, **37**, 844 (1989).