Electroless Gold Plating by Disulfiteaurate Complex

By H. Honma, A. Hasegawa, S. Hotta and K. Hagiwara

Non-cyanide electroless gold plating, using a disulfiteaurate complex, is unsatisfactory because the complex is unstable and easily decomposes. Bath stability was improved by using Na_2SO_3, $Na_2S_2O_3$ and nitrilotriacetic acid as complexing agents; the disproportionation reaction of gold(I) ions was suppressed by the addition of cupferron, bipyridine or $Ni(CN)_2 \cdot 2KCN$. The plating rate ranged from 0.7 to 1.0 μm/hr with sodium ascorbate as a reducing agent. The rate was increased to about 1.5 to 2.0 μm/hr with the addition of sodium ascorbate and hydrazine sulfate. Based on these results, gold wire bondability was evaluated. Gold crystal orientation was influenced by the wire bonding, and high bonding strength was obtained with (220) and (311) preferred orientation gold films.

Gold is widely used in wiring or connecting technology because of the recent trend toward miniaturization of electronic components. Because gold is very expensive, saving gold by selective metallization is becoming increasingly important. Moreover, application of electroless gold plating to a complicated circuit or isolated area with fine lines and small holes is also becoming important. Most earlier electroless gold plating relied on the displacement reaction;[1,2] therefore, thick gold films were not obtained. Accordingly, electroless gold plating based on the autocatalytic reaction is indispensable. Generally, a gold cyanide complex has been used as a metal source, and borohydride or dimethyl amine borane has been used as a reducing agent for the electroless gold plating solution.[3,4]

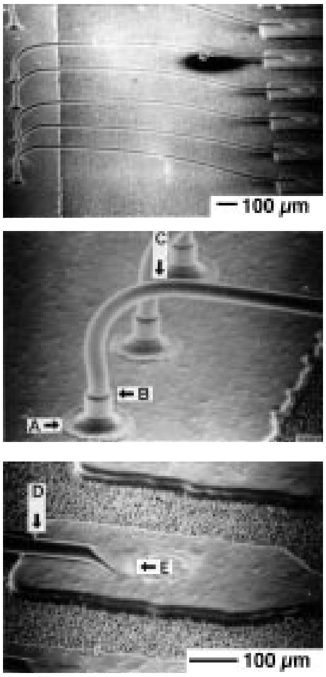

Fig. 1—SEM micrographs of gold wire-bonded area.

The plating bath containing cyanide compounds is not only hazardous but tends to penetrate to the photoresist as well; dissolution of the photoresist results. For these reasons, the non-cyanide electroless gold plating bath has been studied. Several papers related to electroless gold plating reported on the use of disulfiteaurate as a metal source and sodium ascorbate as a reducing agent.[5-13] The bath gradually degrades within several hr, however, and black precipitates are formed in the bath.[14] The purpose of this study was development and application of non-cyanide electroless gold plating to fabricate circuits and electrodes on electronic devices, and to evaluate gold wire bondability.

Table 1
Experimental Process

Alkaline degreasing (40 °C, 5 min)
↓
Rinse (40 °C, 3 min)
↓
Rinse (R.T., 1 min)
↓
10%—H_2SO_4 (R.T., 1 min)
↓
Rinse (R.T., 1 min)
↓
Catalyzing (R.T., 1 min)
↓
Rinse (R.T., 1 min)
↓
Electroless Ni plating (90 °C, 30 min)
↓
Rinse (N_2 agitation, 40 °C, 1 min)
↓
Electroless Au plating (60 °C, 1hr)

R.T.: room temp.

Experimental Procedure

The plating process is shown in Table 1. Plating bath composition and operating conditions of electroless nickel plating and electroless gold plating baths are shown in Table 2 (a and b). To improve bath stability, complexing agents and stabilizers were evaluated.

The thickness of deposited nickel and gold was measured by X-ray fluorescence. Surface morphologies were observed by scanning electron microscope (SEM). Gold wire bondability was evaluated as follows: Gold wire (25 μm dia.) was connected at one point (point A) with heat and ultrasonic waves, then connected to another point (point E), as shown in Fig. 1. The bonding strength was measured and the wire fracture mode was observed, using a tension gauge. Bonding strength of the gold wire is in the order C, B, D, A and E, from the strongest to the weakest value. Also, the codeposited impurities were analyzed by EPMA and the orientation of the plated gold film was measured by X-ray diffraction.

Results and Discussion

Selection of the Complexing Agent

As shown in Eqs. (1) and (2), the stability constant of disulfiteaurate complex ions is much lower than that of gold cyanide complex ions.[15]

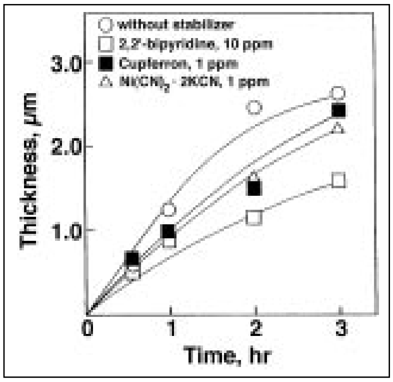

Fig. 2—Effect of stabilizer on plating rate.

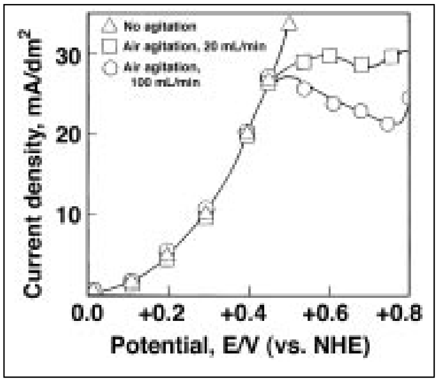

Fig. 3—Polarization curves for anodic oxidation of sodium L-ascorbate under agitation conditions.

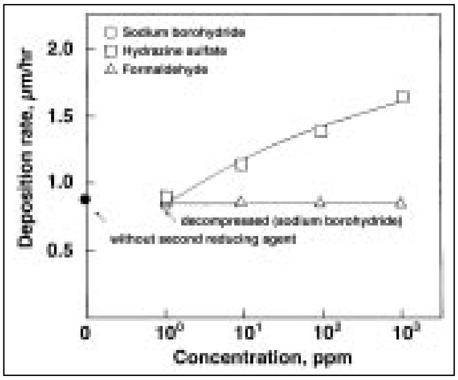

Fig. 4—Relation between concentration of second reducing agents and deposition rate.

$$Au(SO_3)_2^{-3} \leftrightarrows Au^+ + 2SO_3^{-2} \quad [K = 10^{-10}] \qquad (1)$$

$$Au(CN)^- \leftrightarrows Au^+ + 2CN^- \quad [K = 10^{-38}] \qquad (2)$$

Gold(I) sulfite complex ions are unstable from acidic to neutral. Further, HSO_3^- ions are converted to $S_2O_4^{-2}$. These ions act as a strong reducing agent and gold(I) ions are gradually reduced to metallic gold in the solution. Also, free gold(I) ions accumulate at the reaction interface during deposition and a disproportionation reaction takes place according to Eq. (3):

$$3Au^+ \rightarrow 2Au + Au^{+3} \qquad (3)$$

Metallic gold and gold(III) ions are formed in the solution. The bath becomes turbid from metallic gold precipitation and finally decomposes. Accordingly, it is impossible to make up an electroless gold plating bath with this complex only. The study included effects of the various amine compounds for prevention of disproportionation of free gold (I) ions and improvement of bath stability.

Disulfiteaurate complex ions may be changed to $[Au(Am)_2(SO_3)_2]^{-3}$ with amines (Am) by the coordination of amine groups and these complex ions then dissociated according to Eq. (4) and (5). Therefore, the concentration of free gold(I) ions will be greatly suppressed and the stability of the bath may be improved.[16,17]

$$[Au(Am)_2(SO_3)_2]^{-3} \leftrightarrows [Au(Am)2]^+ + 2SO_3^{-2} \qquad (4)$$

$$[Au(Am)2]^+ \leftrightarrows Au^+ + 2Am \qquad (5)$$

Bath stability and the appearance of the deposited gold from addition of various amines is shown in Table 3. Most of the basic baths with these amines decomposed soon after bath make-up. The plating bath life was extended and the brightness of deposited gold was improved by the addition of NTA, however.

The bath with NTA also decomposed after several hr. Accordingly, further improvement of bath stability was studied by the addition of various stabilizers. The results are shown in Table 4. These compounds may form complex ions with gold(I) ions and suppress the disproportionation reaction of free gold(I) ions to increase the bath stability. The appearance of deposited gold was bright; bath stability was increased by the addition of $K_4[Fe(CN)_6]$, cupferron and 2,2'-bipyridine.

Table 2a
Electroless Ni Plating Bath Composition and Conditions

$NiSO_4 \cdot 6H_2O$	0.05 M
dl—Malic acid	0.15 M
NaH_2PO_2	0.30 M
Thiourea	1 ppm
pH	4.5
Temp.	60 °C

Table 2b
Electroless Au Plating Bath Composition and Conditions

$Na_3Au(SO_3)_2$	0.006 M
Na_2SO_3	0.10 M
$Na_2S_2O_3$	0.10 M
NH_4Cl	0.05 M
Na L-ascorbate	0.25 M
Stabilizer	0.1 ~ 100 ppm
pH	6
Temp.	60 °C
Agitation	Air, N_2

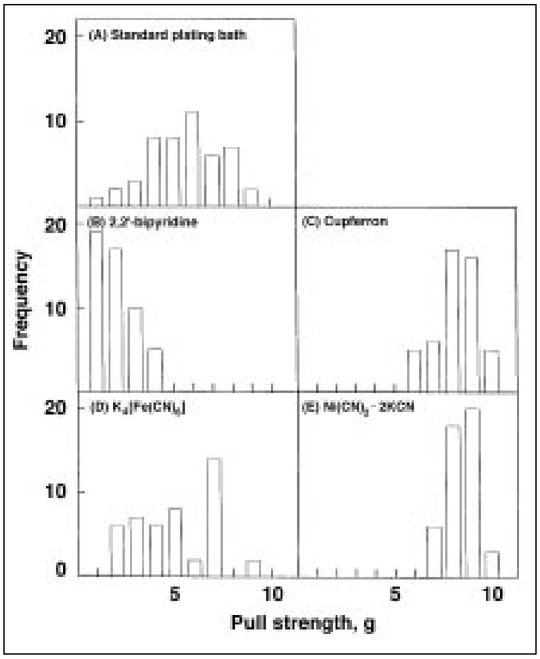

Fig. 5—Bonding strength of gold wire.

Effect of Air Agitation

The rate of electroless gold plating was increased by mechanical agitation. Such accelerating effects may result from diffusion control of the anodic reaction of ascorbate ions. Free gold(I) ions were increased, however, under the low levels of dissolved oxygen (DO) and led to decomposition. Consequently, to decrease the concentration of free gold(I) ions, the effects of air agitation were investigated. The results are shown in Table 5. The plating baths with N_2 agitation were more unstable than the air-agitated plating baths. These results indicate that free gold(I) ions accumulate at the reaction interface and disproportionation proceeds with the N_2-sparged bath, whereas bath stability is

Table 3
Bath Stability and Appearance of Deposited Films

Chemicals	MEA	DEA	TEA	TP	ED	EDTA	DT	TT	NTA	IDA
Value	X	X	C	C	X	B	X	X	A	X

- Monoethanolamine (MEA)
- Diethanolamine (DEA)
- Triethanolamine (TEA)
- Tetraethylenepentamine (TP)
- Ethylenediamine (ED)
- Ethylendiamine Tetraacetic Acid (EDTA)
- Diethylenetriamine (DT)
- Triethylenetetramine (TT)
- Nitrilotriacetic Acid (NTA)
- Iminodiacetic Acid (IDA)

A: Bath stability and appearance of deposited film is good.
B: Bath stability is good, but appearance of film is poor.
C: Decomposition during plating reaction.
X: Decomposition during bath make-up.

Table 4
Effect of Stabilizer on Bath Stability

	ppm			
Stabilizer	**0.1**	**1.0**	**10**	**100**
$K_4[Fe(CN)_6]$	A	A	B	B
$Ni(CN)_2 \cdot 2KCN$	A	A	A	A
2,2'-bipyridine	B	B	A	A
Cupferron	B	A	A	A
2-mercaptobenzothiazole	A	A	C	C
Neocuproin	B	B	A	A
Cytosine	B	B	A	A
Phenanthroline	B	B	A	A

A: Plating proceeds without decomposition.
B: Decomposition after plating.
C: Spotty plating or deplating.

Table 5
Effects of Agitation During Plating

	No agitation	N_2 (mL/min)		Air (mL/min)	
		20	**100**	**20**	**100**
Non-stabilizer	C	X	X	C	C
	[0.66]	[—]	[—]	[1.17]	[1.21]
$K_4[Fe(CN)_6]$, 1.0 ppm	A	C	C	A	B
	[0.93]	[1.24]	[1.65]	[1.19]	[1.27]
$Ni(CN)_2 \cdot 2KCN$, 1.0 ppm	A	C	C	A	B
	[0.69]	[0.73]	[0.88]	[0.80]	[1.03]
2,2'-bipyridine, 10 ppm	B	X	X	A	B
	[0.47]	[—]	[—]	[0.90]	[0.93]
Cupferron, 10 ppm	A	C	C	A	B
	[0.58]	[0.85]	[0.95]	[0.85]	[1.14]

A: Bath stability is improved.
B: Bath stability is improved, but appearance of deposited film is poor.
C: Decomposition after plating.
X: Decomposition while plating.
[ ]: Deposition rate [µm/hr]

increased because of re-oxidation of gold(I) ions by air agitation. No uniform film was obtained, however, under vigorous air agitation (more than 20 mL/min).

Effects of the Second Reducing Agent

Figure 2 shows the deposition rate, which was almost constant for three hr. Figure 3 shows the relation between air agitation and the anodic polarization curves of sodium ascorbate. Oxidation current increased with air agitation. Increases in the oxidation current indicate that the anodic reaction of ascorbate ions is accelerated by air agitation. Consequently, the second reducing agents for prevention of self-oxidation of ascorbate ions were investigated. As shown in Fig. 4, formaldehyde did not show the acceleration effect.

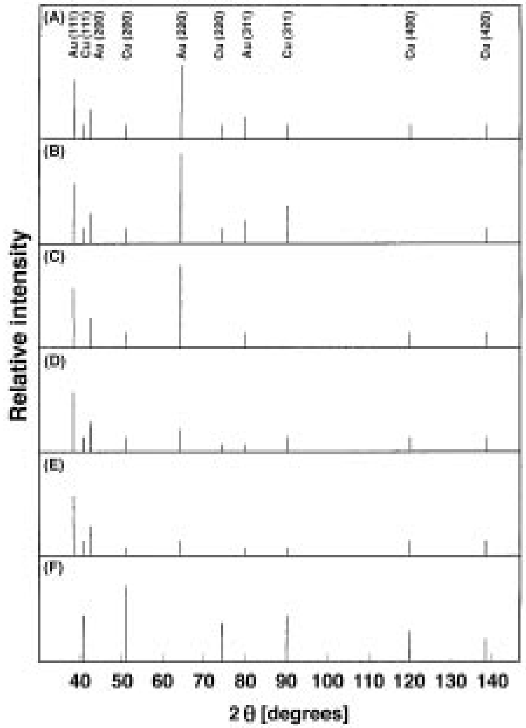

Fig. 6—X-ray diffraction patterns of electroless gold deposits. (A) $Ni(CN)_2 \cdot 2KCN$, (B) cupferron, (C) $K_4[Fe(CN)_6]$, (D) 2,2'-bipyridine, (E) without stabilizer, (F) electroless Ni deposit.

The bath decomposed instantly with the addition of sodium borohydride. On the other hand, the acceleration effect was confirmed by the addition of hydrazine.

Evaluation of Wire Bonding

Bonding strength of gold wire from the addition of each additive is shown in Fig. 5. Fracture between gold wire and deposited films was not observed, but wire bonding strength was different for each stabilizer. The bath with cupferron or $Ni(CN)_2 \cdot 2KCN$ showed from 7 to 10 g/25 µm dia. On the other hand, the bath with 2,2'-bipyridine showed only 2 g/25 µm dia.

To investigate the difference in bondability between the additives, the surface morphology and crystal orientation were observed. No significant differences of morphology and impurity content in the films were determined by SEM and EPMA. Crystal orientation, however, greatly influenced bondability. The crystal orientation of deposited gold films was measured by X-ray diffraction. The results are shown in Fig. 6. Good bondability was obtained with (220) and (311) preferred orientation gold films.

Conclusions

An electroless gold plating process, using disulfiteaurate complex, was investigated. Bath stability was increased by the addition of Na_2SO_3, $Na_2S_2O_3$, and NTA. Moreover, the addition of stabilizers, such as $K_4[Fe(CN)_6]$, $Ni(CN)_2 \cdot 2KCN$, cupferron and bipyridine greatly improved bath stability.

Bath stability was also improved by air agitation. Stability improvement by addition of stabilizers and air agitation was based on suppression of the disproportionation reaction of gold(I) ion.

High gold-wire-bonding strength was obtained from the bath containing $Ni(CN)_2 \cdot 2KCN$ or cupferron as a stabilizer.

Deposited gold crystal orientation also affected gold wire bonding strength. High bonding strength was obtained with (220) and (311) preferred orientation gold films.

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