Preparation of Anisotropic Conductive Particles By Electroless Plating

By K. Hagiwara, J. Watanabe & H. Honma

The problem of connection reliability with large-scale integrated circuits was studied via preparation of conductive particles from electroless nickel solutions. Uniformly covered particles were obtained from an electroless nickel bath, with glycine as a complexing agent. Uniformity was further improved by the addition of a cationic surfactant in the plating bath.

Connection reliability between LSI and electronic devices is increasingly important, especially with the recent trend toward miniaturization of electronic devices. Generally, solder is applied to connections between ICs and circuits. Recently, tape automated bonding (TAB) or flip-chip technologies have been employed for surface mounting of LSI circuitry. In this case, contact reliability between IC chips and electrodes is essential. Solder cannot be applied to chip-on-glass (COG) bonding, however, because cracks in the glass propagate during the soldering steps because of thermal stress. Accordingly, mechanical solderless chip packaging, using small gold bumps and/or conductive resin particles, is applied to contact surfaces between electrodes and circuits, as shown in Fig. 1.1-4 Because the resin balls are nonconductors, an electroless plating process has been applied to provide conductivity. In this paper, we report the preparation of conductive particles, using electroless nickel plating as an underlayer for gold.



Fig. 1—Chip-on-glass (COG) process with conductive particles.

Experimental Procedure

The deposition rate of fine particles is accelerated because their specific surface area is large. Decomposition reactions tend to occur, therefore, when conventional batch processes are used. Accordingly, nickel was plated on the particles via a dropping apparatus, as depicted in Fig. 2. The composition and operating conditions of the electroless nickel plating bath used are listed in Table 1. The dropping solution was divided into concentrated metal solution (A) and reducing agent with sodium hydroxide (B). These solutions were added continuously into the 100-mL dispersing solution. Nickel, hypophosphite and phosphorous acid concentrations were measured by ICP and isotachophoresis (IP). Polystyrene resin balls (7 μ m in diameter, 1.02 g/cm³) were used as sample particles. Pretreatment steps were as shown in Table 2. Surface morphologies after plating were observed by Scanning Electron Microscope (SEM).

Results & Discussion

Initial Plating Behavior

It is considered that onset of the deposition reaction and uniformity of deposited nickel films on the polystyrene particle surfaces depend on the absorption amounts and activities of the palladium catalyst. The particles with low amounts of active catalyst tend to have the catalyst redissolve into the plating bath as palladium ions, leading to spontaneous bath decomposition. It is important, therefore, to accelerate absorption of palladium by reducing agents. The plating reaction is greatly influenced by the acceleration step. If the



Fig. 2—Schematic diagram of dropping apparatus.



Fig. 3—Plating reaction with and without acceleration by hydrazine.



Fig. 4—Relation between plating time and Ni concentration for various complexing agents: (a) \blacktriangle dl-malic acid; (b) \blacksquare sodium tartrate; (c) \blacklozenge glycine; dashed line is calculated value without reaction.



Fig. 5—Relation between plating time and Ni concentration for several values of pH: (a) \oplus pH 5; (b) \blacksquare pH 6; (c) \blacktriangle pH 8; dashed line is calculated value without reaction.



Fig. 6—Effect of dissolved oxygen (DO) in plating solution: (a) mechanical agitation (DO 8 ppm); (b) \bullet air purging with mechanical agitation (DO 10 ppm); (c) \blacktriangle N₂ purging with mechanical agitation (DO 2 ppm); dashed line is calculated value without reaction.



plating reaction proceeded for 5 min without acceleration, the plating bath would become unstable and finally decompose, as shown in Fig. 2. On the other hand, plating reaction started within 60 sec., by the acceleration treatment with hydrazine, proceeded without bath decomposition.

The acceleration effect of the reaction is considered based on the following reactions:

$N_2H_4 \longrightarrow [N_2H_4]_{ads}$	(1)
$[\tilde{N}_2H_4]_{ads} \longrightarrow [\tilde{N}_2H_3]_{ads} + H_{ads}$	(2)
$[N_2H_3]_{ads} \longrightarrow N_2 + 3H_{ads}$	(3)
$H_{ads} + OH_{ads} \rightarrow H_2O + e^{-1}$	(4)

Adsorption and dehydrogenation of hydrazine on the palladium catalytic sites are accelerated and shortened for the induction time of electroless nickel plating. In this way, the plating reaction proceeded smoothly without decomposition.^{5,6}

Selection of Complexing Agent



Uniformity of the deposited nickel on the particles was greatly influenced by the plating bath composition and operating conditions. Complexing agents in the plating solution influence the bath stability and uniformity of deposition on the particles. The plating behavior and

—— 10 μ m

uniformity were investigated, therefore, by the continuous dropping method and by changing complexants. The results are shown in Fig. 3. The plating rate was very slow for about 20 min at the beginning; after that, the plating reaction was rapidly increased by dl-malic acid or sodium tartrate as complexing agents, and many nodule deposits can be seen on the particles (Fig. 4a,b). On the other hand, the plating reaction proceeded smoothly, and uniform film on the particles was obtained with glycine as a complexing agent (Fig. 4c).

Optimum Plating Conditions & Effect of Surfactants The uniformity of deposited films also depends on the pH of



the plating bath.^{7.8} Nickel concentration changes for various values of pH are shown in Fig. 5, as well as deposited surface morphologies of particles. Many undeposited areas can be observed on the particles at pH 5, because the plating rate was very slow. The nickel film became uniform by deposition at pH 6. Nickel

hydroxide was formed in the plating bath, however, with

decomposition at pH 8 and coagulated film occurring on the particles.

Dispersion of the particles is also greatly influential in producing a uniform nickel deposit on the particles; therefore, several methods of agitation were evaluated. As can be seen in Fig. 6, particles were stuck together by mechanical agitation. The plating reaction proceeded smoothly, however, because the activity of the plating bath was increased by the lowering of the dissolved oxygen level.

Further improvement of the effect on uniformity of the various surfactants in the plating bath was investigated. As

Table 1

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Bath Composition & Open	rating Conditions
Dispersing Solution	
Complexing agent	0.1 mol/L
NaH,PO, H,O	0.2 mol/L
pH (adjusted with NaOH)	6
Temp	70 °C
Agitation	N_2 or air
	mechanical
Bath volume	100 mL
Dropping Solution	
A: concentrated metal solution	
NiSO ₄ ·6H ₂ O	1.0 mol/L
B: reducing agent (with pH adjustm	ent) solution
NaH ₂ PO ₂ ·H ₂ O	2.0 mol/L
NaOH*	$1.0 \sim 3.0 \text{ mol/L}$

Dropping rate (both A and B) 3.0 mL/min * pH is constantly adjusted by changing NaOH concentration.

Bath Loading per 100 mL

in Bouung per 100 mB	
Polystyrene resin particles (7 µm dia.)	2.5 g
Number of particles per bath	1.4 x 10 ¹⁰
Area/volume ratio	2100 dm ² /

Table 2

 dm^{2}/L

Pretreatment Process

Etching (60 °C, 10 min) [CrO₃, 10 g/L; H₂SO₄, 700 g/L; H₂O, 300 mL] Water rinse (1 min) Conditioning (3 min) [PEG-1000, 0.1 g/L] Sensitizing (3 min) [SnCl₂, 1.0 g/L] Water rinse (1 min) Activation (3 min) [PdCl₂, 0.05 g/L, pH 3] Water rinse (1 min) Acceleration (3 min) [Hydrazine, 0.05 g/L]

shown in Fig. 7, the deposited particles from addition of a cationic surfactant to the plating bath showed good surface morphology.

Summary

The preparation of conductive particles via electroless plating, using a continuous dropping process was investigated. It was confirmed that the induction time was greatly shortened by using hydrazine as an accelerating agent.

Uniformity of the deposited nickel on the particles was dependent on the complexing agent in the plating bath. Uniformly covered particles were obtained from an electroless nickel bath, with glycine as a complexing agent. Uniformity was farther improved by the addition of a cationic surfactant in the plating bath.

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10 µ m

Fig. 7—Effect of the various surfactants: (a) basic bath; (b) anionic; (c) non-ionic; (d) cationic.

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Hagiwara

Honma

About the Authors

Ken Hagiwara holds BS and MS degrees in chemical engineering from Kanto Gakuin University, Japan.

Jyoji Watanabe is a graduate student in chemical engineering at Kanto Gakuin University.

Dr. Hideo Honma is professor of chemical engineering at Kanto Gakuin University, 4834 Mutsuura-cho, Kanazawaku, Yokohama-shi, Kanagawa 236, Japan. He received BS and MS degrees in chemical engineering from Kanto Gakuin University and a PhD from the University of Osaka Prefecture. He has been working in electrolytic and electroless plating for more than 30 years and has published more than 60 papers in his specialties.