Application of Precision Filtration To an Electroless Copper Plating Bath

By T. Fujinami & H. Honma

Electrolytic and electroless plating are becoming extremely important for forming functional thin films. Printed circuit boards are indispensable as elements of electronic equipment, and the boards are shrinking in size. Accordingly, the full additive process can be attractive as a substitute for the subtractive process. Extraneous deposition occurs easily on the circuits, however, when copper is deposited using the additive process. The sulfate and formate ions accumulated during the plating reaction are the cause of extraneous deposition, or plate-out. Nascent hydrogen is also a possible cause inasmuch as extraneous deposition develops with the evolution of hydrogen gas, as shown in Fig. 1.[1] Extraneous deposition still occurred, however, even when these related factors were eliminated. Fine inorganic particles in the plating bath are also a possible cause of extraneous deposition.[2] Accordingly, elimination of the extraneous deposition by filtration was investigated, as well as the inhibiting effect of the filtering media.

Experimental Procedure

Preparation of Plating Bath

Basic bath composition and plating conditions of an electroless copper plating bath are shown in Table 1. Sodium formate and sodium sulfate were added to the plating bath as the reaction products to simulate the conditions that cause extraneous deposition.

Filtration

The plating solution was circulated between the plating bath and the filter at a constant rate of 100mL / min. Glass epoxy substrates (having 130 µm line width and 187.5 µm thickness) were used as samples. The extraneous deposition was observed with an optical microscope after plating.

Measurement of Fine Particles

Samples of each plating solution were collected regularly and particles larger than one micron were measured. Chemical composition of the particles was analyzed by electron probe micro analysis (EPMA).

Physical Properties of Deposited Copper

The ductility of the deposited copper coatings was measured and surface morphologies were observed by scanning eleatron microscopy (SEM) after peeling copper foil from a test plaque. Also, the deposition inhibition effect of the filtering media was investigated by using wound vs. profile filters.

Results and Discussion

Effect of Continuous Filtration

Formate and sulfate ions accumulated from the main and side reactions of the electroless copper plating. The simulated spent bath represented five turnovers. Filtration flow rate was kept at 100mL/min. Conditions of extraneous deposition on the basis of pore size variation of the filter were monitored. The result is shown in Fig. 2. Extraneous deposition patterns were observed in unfiltered baths. Deposition of copper metal was observed on the resist surface; on the other hand, the extraneous deposition was inhibited by the continuous filtration. Extraneous deposition was inhibited significantly as the pore size of the filter became smaller. Accordingly, the inhibiting effect on extraneous deposition as the result of filtering media action was considered proved.

Table 1
Bath Composition & Operating Conditions

Composition	Concentration
$CuSO_4$ $5H_2O$	0.3 M
EDTA - 4H	0.24 M
HCHO	0.20 M
2,2'-bipyridine	10 mg/L
PEG-1000	100 mg/L
HCOONa	1.30 M (90 g/L)
Na_2SO_4	0.17 M (25 g/L)
Conditions	
Volume	1 L
Temp	60 °C
pH	12.5
Load factor	1.0 dm /L
Agitation	air

Measurement of Particles & Determination of Chemical Elements In the Bath

In this investigation, the number of insoluble fine particles in the plating bath and their chemical constitution were examined. The results are shown in Table 2. Particle quantities of approximately 2,000,000 were found in a newly prepared bath without filtration, and about 3,000,000 were detected in the simulated aging bath. Particle numbers sharply decreased to the tens-of-thousands level with filtration; however, particle quantities gradually increased during the plating reaction. Therefore, application of continuous filtration is desirable to inhibit extraneous deposition. Chemical elements of particles in the plating bath were analyzed by EPMA. The major chemical constituents of the particles were found to be Si, Al, Mg and Na, as shown in Fig. 3. These inorganic particles are regarded as a possible cause of extraneous deposition. Fine particles such as Al or Fe in the plating bath tend to form oxyhydrates and hydroxides. Complexing agents

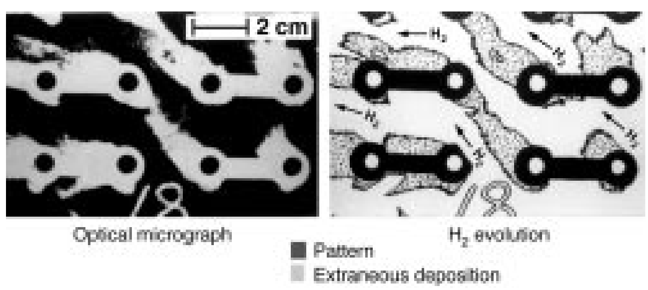


Fig. 1—Extraneous deposition together with direction of hydrogen evolution.

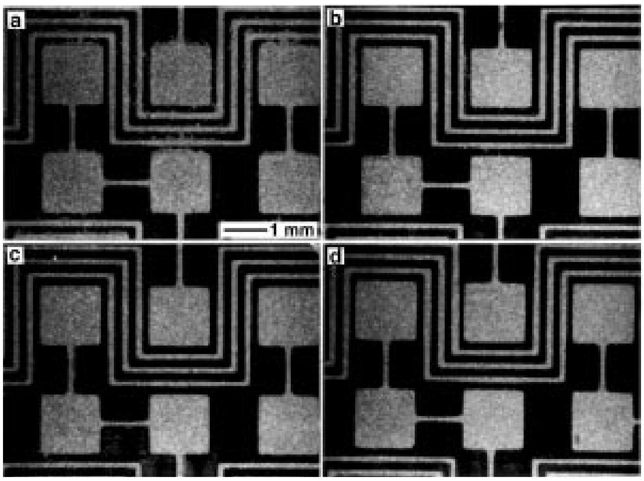


Fig. 2—Effects of continuous filtration: (a) without filtration; (b) pore size 70 µm; (c) pore size 10 µm; (d) pore size 0.6 µm.

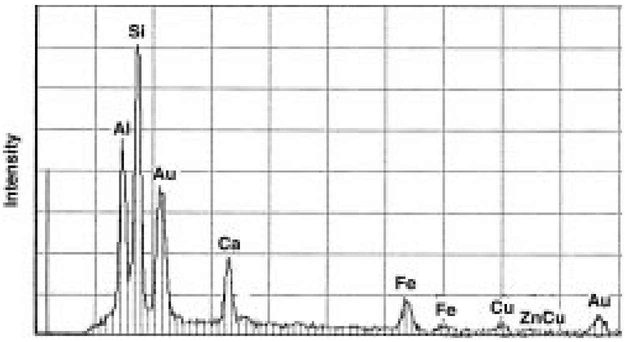


Fig. 3—Chemical analysis of insoluble particles in the electroless copper solution.

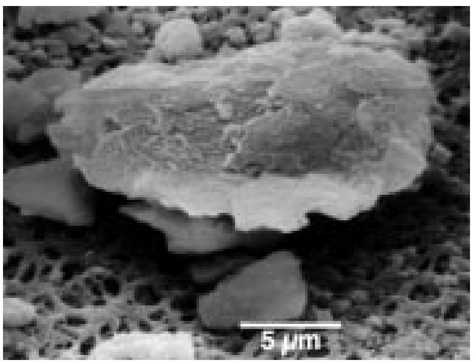


Fig. 4—Fine particles on a filter. SEM image for EPMA pattern of Fig. 2.

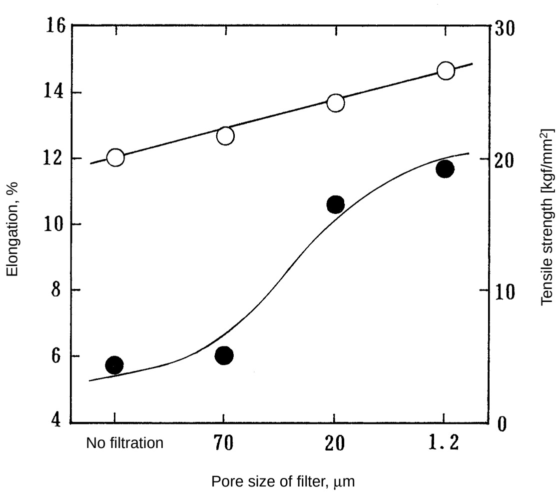


Fig. 5—Effect of filter pore size on elongation and tensile strength.

Table 2
Numbers of Particles in Electroless Copper Bath
Filter pore size: 0.6 µm

	Bath make-up (without filtration)	**Particle count/100 mL** After 2 hr plating
New bath	160,000	(filtration) 2,300
		(without filtration) 180,00
Bath with 5 turnovers	260,000	(filtration) 3,700
		(without filtration) 330,000

and wetting agents in the bath tend to be adsorbed on silicon particles; accordingly, these particles become negatively or positively charged. As a result, they are adsorbed on the reaction interface of the copper substrate. The particles are also trapped in the deposited copper films during the plating reaction.[3] These fine particles are proved to be a cause of extraneous deposition, as shown in Fig. 4. Extraneous deposition progresses as the plating reaction continues.

Physical Properties Evaluation Of Deposited Copper

If inorganic fine particles can be removed with continuous filtration, extraneous deposition will be inhibited. Accordingly, filtration conditions were evaluated because they may affect the physical properties of the deposited copper. Without filtration, the ductility of deposited copper is approximately six percent. Pore size of the filter medium was reduced; the effect is shown in Fig. 5. Ductility was improved; its value reached 12 percent as the pore size decreased. The surface morphology of deposited coatings was also observed. In unfiltered solutions, much extraneous deposition was observed, as shown in Fig. 6. As an additional benefit, defects in the coatings decreased by applying filtration, and the deposited films became smooth.

Inhibition of the deposition reaction in or on the filter medium is also necessary to extend the life of the filter.

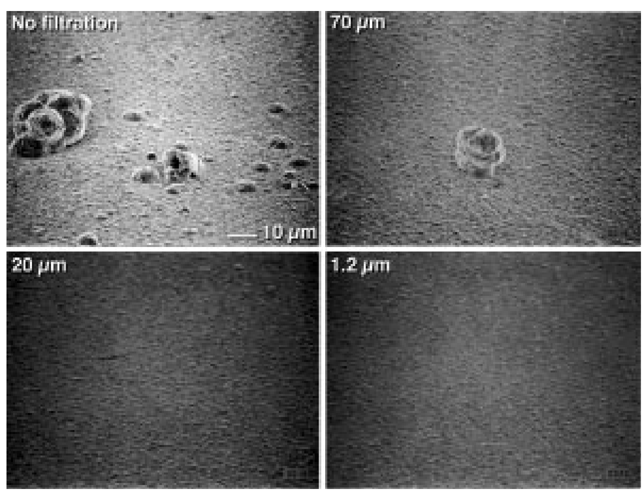
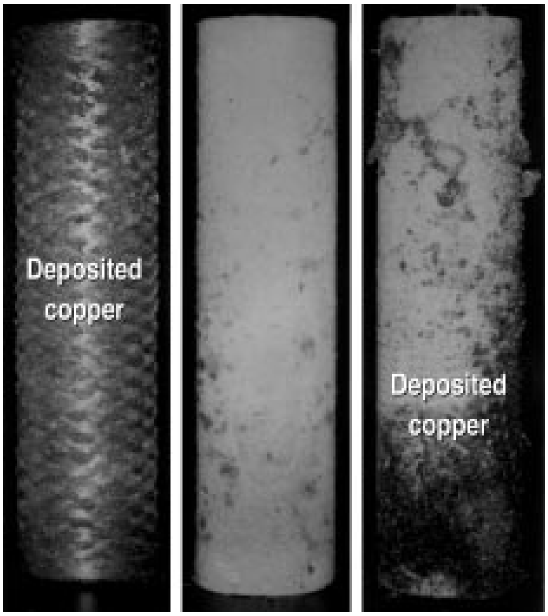


Fig. 6—Effect of extraneous deposition as a function of filter pore size.



a b c

Fig. 7—Performance comparison of filter media: (a) wound filter; (b) profile filter, high flow rate; (c) profile filter, low flow rate.

Figure 7 shows the performance comparison of filter media, using the wound filter and the profile filter. Generally, filter fiber diameter is not fixed, and an internal void ratio exists, scattered in the wound filter. Accordingly, the flow rate is not constant in the filter and plating solution tends to stagnate inside the filter; therefore, electroless plating reaction occurs at the vicinity of the wall of the filter medium (Fig. 7a). On the other hand, flow rate can be maintained at a constant high value and the internal deposition is inhibited by using the profile filter (Fig. 7b). Deposition was pronounced, however, if the flow rate was less than 50 mL/min (Fig. 7c).

The oxidation reaction of formalin is shown in Fig. 8. A glassy carbon electrode was used as a rotating disk electrode. Oxidation current was measured after being catalyzed with palladium on the glassy carbon electrode. The oxidation reaction of formalin was inhibited by increasing the rotation speed of the disk electrode. Onset of the potential related to the plating reaction may therefore be shifted toward more noble potentials, indicating that the plating reaction on or in the filter medium was inhibited with increasing flow rate.

Summary

The effect of deposition inhibition through precision filtration and the physical properties of electroless copper were examined. If continuous filtration was applied during plating, extraneous deposition was greatly inhibited. When the pore size of filtering media was reduced, the physical properties of the copper coating improved because foreign particles (impurities) in the plating solution were removed by continuous filtration. Deposition inside the filtering media was reduced with increasing flow rate.

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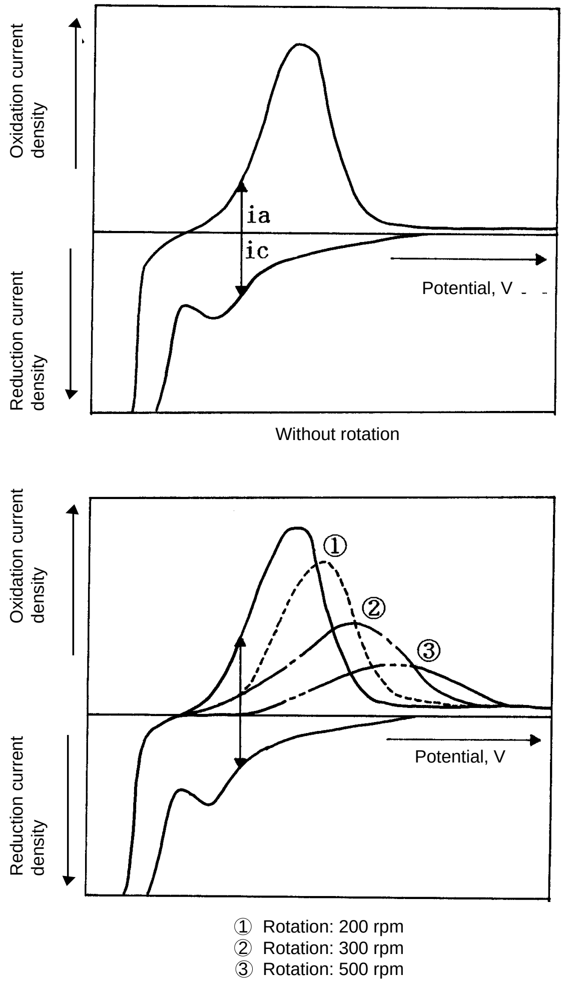

Fig. 8—Mixed potentials for electroless copper bath.

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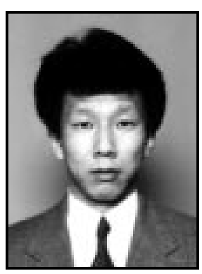

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