Mechanistic Study of Direct Copper Plating Using a Pd Catalyst & S Ligand

by H.S. Chen, Y.J. Huang, & C.C. Wan*

The mechanism of direct plating using a Pd/S catalyst was investigated based on plating performance and compared to a system with a graphite colloid film. The results indicate that plating occurred as a result of the bridging-ligand property of the sulfur atoms rather than the surface conductivity of the Pd/S layer. The structure of the Pd/S compounds formed after dipping in Pd^{+2}, S^{-2} and SO_4^{-2} baths was also identified by IR spectroscopy and XRD. The major compound was Pd_4S instead of PdS.

Autocatalytic electroless copper plating has been used in printed circuit board manufacturing for over 30 years. This process is facing serious environmental problems since it consumes vast amounts of formaldehyde as a reducing agent and several kinds of chelating agents. Alternative processes have been proposed, which can bypass this electroless step and directly electroplate copper on the substrate. They are usually referred to as direct plating or direct metallization.

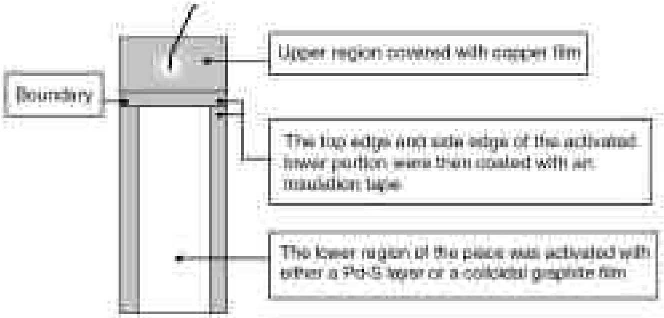

Fig. 1—Diagram of test sample to verify the insulation property of Pd/S film.

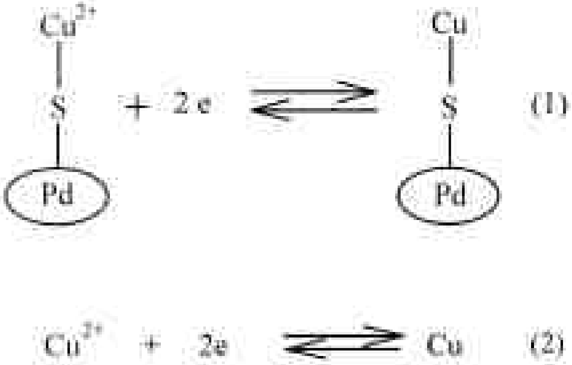

Fig. 2—Dual-reaction model for direct plating via Pd/S catalyst.

Nuts & Bolts: What This Paper Means to You

This work deals with a potential replacement for the conventional formaldehyde-based electroless copper process. The goal was to avoid the toxicity problems of the formaldehyde. This process involves direct copper plating using a palladium/sulfur catalyst. Plating did occur, and the details of what went on in the process are described here. The cliché about "out-of-the-box" thinking applies.

One widely-used proprietary process**, like conventional electroless copper, uses a Pd/Sn colloid as an activator.[1-4] However, it replaces the electroless copper step with an "enhancement" step, a sulfide dip. After this step, the substrate can be directly electroplated. Since this process can replace the conductive electroless copper, it is reasonable to assume the major function of the enhancement step is to form a conductive palladium sulfide (Pd/S) film on the substrate surface.[5]

Yang, et al.[6] first pointed out the possible weakness of this notion and instead proposed a dual-reaction model. Chiang, et al.[7] later studied the mechanism of Pd/S formation and found that it did not readily form after dipping in the sulfide solution. Stable PdS appeared only after immersion in the plating bath containing the sulfate ions. In Chiang's paper, the existence of PdS was identified by IR spectroscopy and characteristic peaks were found at 1110, 617 and 423 cm^{-1}. Recently, we questioned the validity of using these peaks to identify PdS. The aim of this paper, then, is to continue the study of Pd/S formation and its function in the direct plating process.

If sulfate ions were primarily responsible for the formation of stable PdS,[7] it would follow that direct plating could not proceed if the copper sulfate bath were replaced by a pyrophosphate bath. In this study, we also compared the plating performance of the proprietary process to another direct plating process based on a conductive carbon colloid***. Any difference should show any intrinsic difference in the plating mechanisms of the two direct plating processes.

Experimental

Confirmation of Bridging-ligand Concept For Direct Plating Using a Pd/S Catalyst

If, instead of assuming a conductive Pd/S layer on the non-conductive substrate, direct plating proceeds through

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** *Crimson Process, Shipley Co., Newton, MA.*

*** *Shadow Process, Electrochemicals, Inc., Maple Plain, MN.*

a dual-reaction model, there would then be a basic difference between direct plating with a Pd/S catalyst and with a conductive colloid carbon.

Accordingly, we designed a test to check the surface conductivity of the Pd/S film. Pieces of PCB laminate were used as test samples as shown in Fig. 1. The upper portion, 1.0 cm long and 2.0 cm wide (0.4 x 0.8 in.), contained a conductive copper film on its surface for connection to the external current source. The lower region (3.0 cm; 1.2 in. long) was a bare FR-4 plate which was later covered with either the Pd/S layer or the colloidal graphite film as the activation film.

The top and side edges of the lower portion were then coated with an insulating film (adhesive tape). The insulation film on the sides produced a more uniform current distribution in the center of the panel. The insulation film near the top served as a boundary between the upper and lower regions.

The upper region including the boundary was not immersed in the solution and therefore copper could not deposit thereon. The lower portions of the test pieces were immersed in a copper sulfate solution ($CuSO_4.5H_2O$, 40g/L; H_2SO_4, 50mL/L) for direct copper plating. A constant potential was applied by a potentiostat. If the activation film (Pd/S or graphite) was conductive, then the whole surface was conductive and current could transfer from the top copper film to the lower region and plating would commence. If the activation layer was not conductive, then the current could not pass from the upper copper film to the lower part and plating could not start. Determining whether or not direct plating could be triggered showed whether or not the particular process surface activation layer was conductive. The chemicals and formulations used are given in Table 1.

Identification of the Structure of Pd/S

Chiang, *et al.*[7] confirmed the existence of PdS by IR spectroscopy and claimed the formation of PdS was made possible by the existence of sulfate ions. If sulfate ions were the only agent capable of effecting this reaction, switching the copper plating bath from a conventional acidic copper bath to a pyrophosphate copper bath ($Cu_2P_20_7$, 24.8 g/L; $H_4P_20_7$, 60 mL/L) should stop the direct plating. We did a comparative test to verify this observation.

In addition, the IR peaks confirming the presence of PdS were reported to be 1106 and 615 cm^{-1}.[7] However, the IR peak reported in the literature[8] was 430 cm^{-1}. Accordingly, we repeated the IR spectroscopy studies to identify the Pd/S compound.

Results & Discussion

Confirmation of Dual-reaction Model

The rate of lateral growth of copper by direct copper plating depended on the activation procedure. The results are shown in Table 2.

The graphite colloid process was used for comparison. The surface conductivity was measured by a four-point probe. The surface conductivity with the graphite colloid as an activator was much higher than that obtained with the Pd/S activator by four orders of magnitude. Yet the two processes produced comparable plating rates, which again implied that direct plating using a Pd/S catalyst must have been promoted by some mechanism not directly related to the surface conductivity. In fact, the surface conductivity of the substrate without the enhancement step was only 1.38 MΩ, and the surface could still be directly plated although the rate was much lower than that with enhancement.

Table 1
Chemicals & Formulations Used in (a) Pd-S Process; (b) Graphite Colloid Process

Pd-S Process	
Cleaning	Proprietary cleaner*, 15 mL/L
Microetch	H_2O_2, 100 mL/L; H_2SO_4, 250 mL/L
Pre-dip	NaCl, 280 g/L
Activation(Conc.)	$PdCl_2.2H_2O$, 10 g/L $SnCl_2.2H_2O$, 500 g/L HCl, 300 mL/L
Acceleration	NaOH, 0.4 g/L
Enhancement	$Na_2S.xH_2O$, 0.5 g/L
Electroplating	$CuSO_4.5H_2O$, 40 g/L H_2SO_4, 50 mL/L
Graphite Colloid Process	
Cleaning	Proprietary Cleaner/Conditioner**, 14 vol%
Shadow	Proprietary Colloid***, 50 vol%
Fix	Fixer, 10 vol%
Electroplating	$CuSO_4.5H_2O$, 40 g/L H_2SO_4, 50 mL/L

* *Crimson 5110, Shipley Co., Newton, MA.*
** *Cleaner/Conditioner III, Electrochemicals, Inc., Maple Plain, MN.*
*** *Shadow Colloid II, Electrochemicals, Inc., Maple Plain, MN.*

Table 2
Growth Rate of Copper Deposit

Procedure		**Avg. Growth Rate, cm/min**	**Avg. Surface Conductivity**
Pd/S Process	Activation	1.46	1.38 MΩ
	Acceleration	0	2.58 MΩ
	Enhancement	0.95	3.03 MΩ
Graphite Colloid Process		1.48	117 Ω

This was first discovered by Radovsky.[9] He attributed it to the catalytic activity of palladium. However when the substrate was later dipped in the accelerator solution, the surface conductivity decreased slightly and the plating completely stopped. Interestingly, the plating resumed when the surface was dipped in a sulfide solution although the surface conductivity was found to decrease continuously to 3.03 MΩ. Therefore, this peculiar phenomenon can only be adequately explained by the dual-reaction model previously proposed from this laboratory.[6]

In this model, Yang, et al. proposed that plating proceeds with two reactions in parallel as shown in Fig. 2. The lateral growth of copper on the activated surface was initiated by charge transfer from the palladium through the sulfur ligand to the cupric ion (reaction 1) rather than by conventional copper reduction (reaction 2) which happened only vertically to increase the thickness of copper deposit.

To further verify the mechanism, we used the test sample configuration shown in Fig. 1 to differentiate the graphite colloid and the Pd/S catalyst. The results are shown in Table 3.

If the whole surface were conductive, external current would naturally pass from the connector to the copper film (upper region) and then to the activation film from the boundary down to the lower region (Fig. 1), so plating would start in the lower region covered with the activation film. The copper deposit would then develop downward. In the case of a test piece activated with Pd/S, the current was zero which meant that the current could not pass from the copper film through the Pd/S covered boundary region to the lower region. Therefore, direct plating could not be initiated. This meant that the Pd/S film was highly resistive. However, in the graphite colloid activation, the current (decreasing from 0.02 to 0.01A in Table 3) could easily pass through the conductive graphite film underneath the non-conductive tape at the boundary to the lower region, so the plating proceeded smoothly in the lower region. This simple test can illustrate the basic difference between the plating mechanisms of the two systems. The mechanism of the Pd/S system was chemical in nature as explained previously (Fig. 2) and that of the graphite colloid system was related to the intrinsic conductivity of the graphite film.

Table 3
Direct Plating Results by Pd/S Activation & Graphite Colloid Activation

	Pd/S Activation	Graphite Colloid Activation
Boundary Gap (cm)	0.1	0.1
Applied Voltage (V_{SCE})	---	3.0 – 3.5
Current (A)	0	0.02 – 0.01

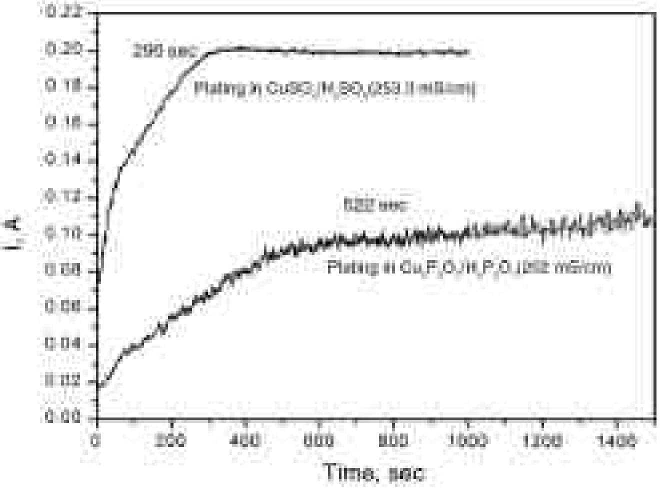

Fig. 3—Direct plating (1.0 V_{SCE}) of Pd/S process with and without dipping in microetch.

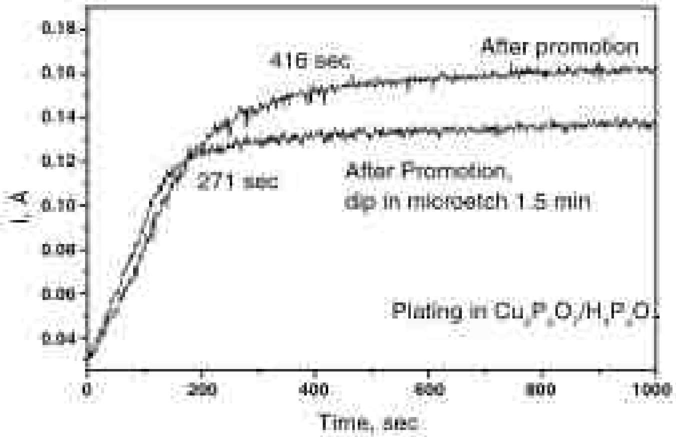

Fig. 4—Direct plating (1.0 V_{SCE}) of Pd/S process with and without dipping in microtech.

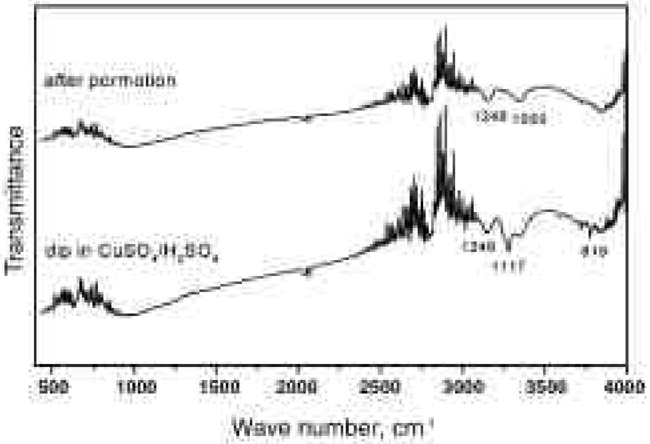

Fig. 5—IR spectrum of Pd/S process after promotion and dipping in plating solution.

Identification of the Structure of Pd/S

Initially, the compound after sulfide immersion was generally believed to be PdS. Chiang, *et al.*[7] further proposed that stable PdS formed only after the substrate was in contact with sulfate ions existing in the plating bath. Accordingly, we first checked the function of the sulfate ions by using a pyrophosphate copper bath instead of the conventional cupric sulfate bath. The copper ion concentration was maintained at 0.16M. The results are shown in Fig 3.

It is obvious that direct plating could proceed in either the acid copper or the pyrophosphate bath. This meant that sulfate ions were not essential in the Pd/S system although the plating rate of the pyrophosphate system was somewhat slower than that of the sulfate bath. The surface was fully covered with a copper deposit in 290 seconds in the sulfate bath versus 522 seconds in the pyrophosphate bath. This is reasonable however, since the pyrophosphate system generally exhibits a slower plating rate, even on conventional conductive substrates.

Although sulfate ions were not found to be essential to the Pd/S process, the possibility remained that they still could possess some sort of promotional effect. In order to ascertain that possibility, we immersed the substrate in a H_2SO_4-containing microetching solution after it had been treated with the sulfide solution. The result is shown in Fig. 4. Indeed, the sulfate ions could accelerate the direct plating rate. Thus, the sulfate bath served both to provide copper ions for plating and to activate the Pd/S film by the existing sulfate ions.

This additional role of sulfate was initially proposed by Chiang, *et al.*[7] They also claimed that stable Pd/S compounds formed only after the substrate was immersed in a sulfate-containing solution. The IR spectroscopy results shown in Fig. 5 indicate that two additional peaks appeared after the surface contacted the acidic copper sulfate bath and these two peaks could be used as an indicator as to whether the surface was directly platable. Chiang, *et al.*[7] actually found that the two peaks disappeared if the sulfide immersion was too long, *i.e.*, over 10 minutes. If stable Pd/S compounds formed right after the sulfide dip, there would be no reason why the PdS could dissolve or dissociate by mere immersion in the sulfide bath for a few extra minutes. Hence, although we are still unsure as to the exact nature of the compound formed after sulfide immersion, we can safely say that a stable PdS had yet to form immediately thereafter and a stable activation film only developed after the surface had contacted the plating bath.

Still, we are not totally confident that the two peaks, 619 cm^{-1} and 1117 cm^{-1}, could represent PdS. The largest peak for PdS reported in the literature is 430 cm^{-1} and most of its absorption peaks should be between 250 and 300 cm^{-1}. Indeed, we used a new PdS standard and found no corresponding peaks as shown in Fig. 6.

Using XRD to check the true identity of the PdS standard used by Chiang, *et al.*,[7] we found the two peaks at 619 cm^{-1} and 1117 cm^{-1} most likely represent Pd_4S.

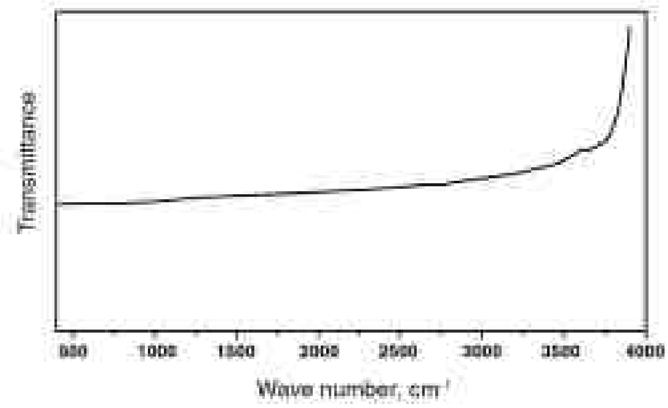

Fig. 6—FTIR spectrum of PdS standard.

Conclusions

1. The mechanism of direct plating by (Pd/S activation) can be explained by a dual-reaction model which differs from a graphite colloid activation system whose mechanism can be explained by surface conductivity.
2. It was found that Pd_4S, instead of PdS, was formed after immersion in sulfate solution. The sulfate ions seemed to have some effect in increasing the plating rate.

References

1. J.J. Bladon, U.S. patent 4,895,739 (1990).
2. J.J. Bladon, U.S. patent 4,919,768 (1990).
3. J.J. Bladon, J. N. Robinson and M. Rousseau, U.S. patent 4,952,286 (1990).
4. J.J. Bladon, U.S. patent 5,007,990 (1991).
5. J.J. Bladon, A. Lamlla, F. W. Lytle, W. Sonnenberg, J.N. Robinson & G. Philipose, *J. Electrochem. Soc.*, **143**, 1206 (1996).
6. C.H. Yang, Y.Y. Wang, & C.C. Wan, *J. Electrochem. Soc.*, **143**, 3521 (1996).
7. Y.Y. Chiang, Y.Y. Wang, & C.C. Wan, *J. Electrochem. Soc.*, **146**, 3255 (1999).
8. D.M. Adams & J.B. Cornell, *J. Chem. Soc. (A)*, 884 (1967).
9. D.A. Radovsky & B.J. Ronkese, U.S. patent 3,099,608 (1963).

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