A Potential Silver Catalyst System for New Generation of Electroless Cu Process as a Palladium Substitution

Lok Lok Liu, Sau Man Ku, Chit Yiu Chan, Kwok Wai Yee

Dow Electronic Materials - The Dow Chemical Company

15 On Lok Mun Street, On Lok Tsuen, Fanling, Hong Kong

liu223680@dow.com

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ABSTRACT

Electroless plating of copper onto insulating substrates is a process broadly applied in the electronics industry for manufacture of printed circuit boards and decorative plating of plastic parts for automotive or consumer appliance. The key step involves surface activation of the dielectric surface for deposition in electroless copper bath. Palladium catalyst, either in its ionic form or metallic form, is most widely used for this purpose. However, the high and volatile unit metal price causes the catalyst solution to be the most expensive part among the electroless process. The economic pressure imposed on manufacturers and consumers would be the major driving force for developing an alternative catalyst system with lower cost.

Previously we have introduced the innovative nano-silver catalyst system such as the physical properties, catalytic performance on conventional electroless copper deposition, and reliability performance in copper-copper interconnects area. [1] In this paper, comparison of silver catalyst with traditional palladium catalyst for MHC process will be described. Further study on deposition profile, microvia coverage and morphology, and reliability performance with liquid-to-liquid thermal shock will be illustrated. In the last section, the concerns on silver migration with silver catalyst applications on printed circuit board will be discussed.

OVERVIEW ON MHC CATALYST

The most commonly used method for activation of non-conductive dielectric substrate region in MHC process is treating the board with palladium-tin (Pd-Sn) colloid catalyst in an acidic medium or ionic palladium catalyst in an alkaline medium. These two types of palladium catalyst share similarity, yet distinct properties in some aspects. Silver catalyst, a novel catalyst to MHC process, would create a new position among the current catalyst systems.

A comparison between Pd-Sn catalyst, ionic Pd catalyst, and Ag catalyst has been illustrated in Table 1. Each type of the MHC catalyst shows advantages and disadvantages in different aspects. Pd-Sn colloid catalyst is the most versatile catalyst and broadly applied with the longest history. However one of the key concerns would be the use of tin (II) chloride and the corrosive nature of the working bath conditions. Strong etching is required for tank maintenance in order to remove the Pd-Sn residues efficiently. Difficulties on the removal of catalyst at non-plated through holes (NPTH) will initiate un-wanted nickel plating during the final finishing step. The disadvantages came from the use of tin (II) chloride can be avoided in ionic Pd catalyst. The process window for maintaining good reliability is wider for ionic Pd catalyst process. Ag catalyst has absolutely advantages over the metal unit price, around 37 times cheaper than palladium. Higher catalyst adsorption (6-10 ug/cm^2) is required to enhance the surface activation ability. Excellent reliability can be maintained at a wide process range. Due to the non-catalytic nature of Ag catalyst in the electroless nickel bath, there will be no NPTH concerns in the final finishing step.

TABLE 1: MHC CATALYST COMPARISON

Catalyst	Pd-Sn Colloid	Ionic Pd	Ag
Metal Price* (USD/oz.)	697	697	19
Stabilizer	$SnCl_2$	Organic stabilizer	Biodegradable stabilizer
Catalyst Adsorption (ug/cm^2)	0.4-0.9	0.2-0.3	6-10
Working Bath pH	<1	9-10	4.25-4.75

Equipment Maintenance	Strong Etching (H_2O_2/ HCl)	Strong Etching (H_2O_2/ HCl)	Soft Etchin (H_2O_2/ H_2SC
Process Window for Good Reliability	Fair	Wider	Wider
NPTH concerns	High	Fair	No concerr

*Retrieved on 22nd Aug 2016

Silver catalyst shares similar characteristics of both Pd-Sn and ionic Pd catalyst. The key advantages would be the low metal price and excellent reliability performance, which allows silver catalyst to be placed at a unique position among the other palladium catalyst for MHC process. Performance of silver catalyst on deposition profile, microvia coverage and morphology, and reliability study with liquid-to-liquid thermal shock will be described in the next section.

SILVER CATALYST PERFORMANCE

Catalytic performance on conventional electroless copper deposition and reliability performance in copper-copper interconnects area have been previously published. [1] In this section, further studies on deposition profile of Silver Catalyst process, the microvia coverage and morphology, and the reliability performance by liquid-to-liquid thermal shock test will be described.

Deposition profile

Copper thickness along deposition time was studied on 370HR epoxy surface treated with MHC process applying silver catalyst. Nine pieces of 370HR panel (5cm x 5cm) were immersed into an activated copper bath at t = 0, and one panel was taken out, respectively, after 1, 2, 3, 4, 5, 7.5, 10 and 15 minutes of plating time. For the measurement of copper thickness, X-ray fluorescence (XRF) technique was employed. (XRF Model HITACHI FT9500X XRF Coating Thickness Gauge). Backlight (BL) was graded on a scale of 0 – 5 under optical microscope where light passes through from the back of the holes. An average of 10 holes was evaluated for BL for each type of laminate.

Silver catalyst adsorbed on substrate surface has successfully initiated electroless copper plating within the first 5 minutes of deposition process, resulting in nearly full copper coverage on both epoxy and glass. (Figure 1) Excellent backlight rating of 4.5 or above can be attained in 10 minutes of plating time. (Graph 1) As the plating continued, a desirable copper thickness of 0.4 to 0.6 um was achieved at 15 minutes. (Graph 2)

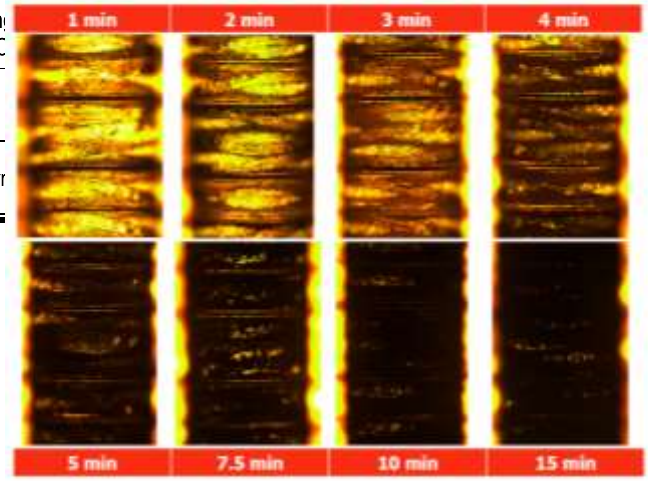
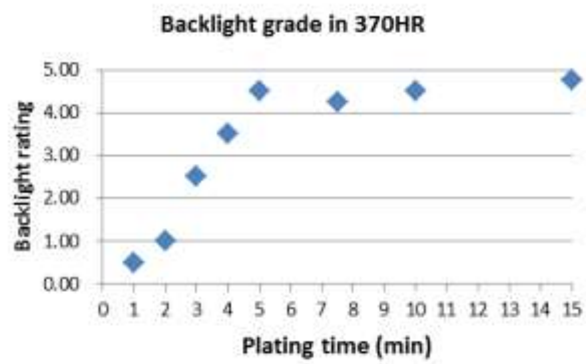
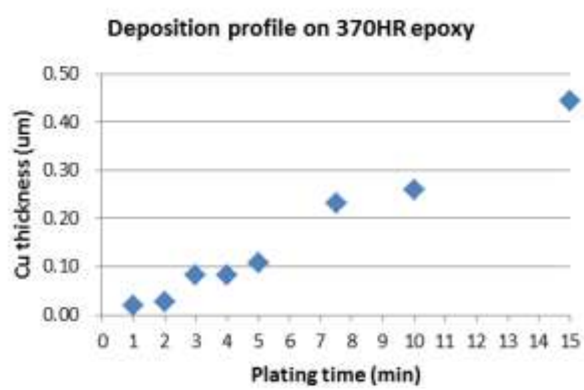


FIGURE 1. BACKLIGHT IMAGES IN 370HR LAMINATE THROUGH-HOLE ALONG DEPOSITION PROCESS



GRAPH 1. BACKLIGHT RESULTS IN 370HR LAMINATE THROUGH-HOLE ALONG DEPOSITION PROCESS



GRAPH 2. THICKNESS OF COPPER DEPOSITED ON 370HR EPOXY SURFACE ALONG METALLIZATION PROCESS

Microvia Coverage and Morphology

Electroless copper coverage and morphology were studied in laminates with both through-holes and microvias. The test panels were first prepared with MHC process applying silver catalyst. The through-holes were routed from the test panels and cross-sectioned to the middle of the holes by manual grinding.

Coverage in microvias was obtained by SEM and FIB examinations. Morphology was evaluated by optical microscope in front light mode or by SEM inspection. For SEM sample preparation, microvias were cross-sectioned by a Cross-section polisher JEOL CP-09010. (SEM, FIB model & manufacturer FIB-SEM Quanta 3D FEG 200)

Examination under SEM shows that full copper coverage was achieved in blind microvia. (Figure 2) The copper growth followed the post-desmear texture of epoxy surface, indicating a uniform and smooth deposition.

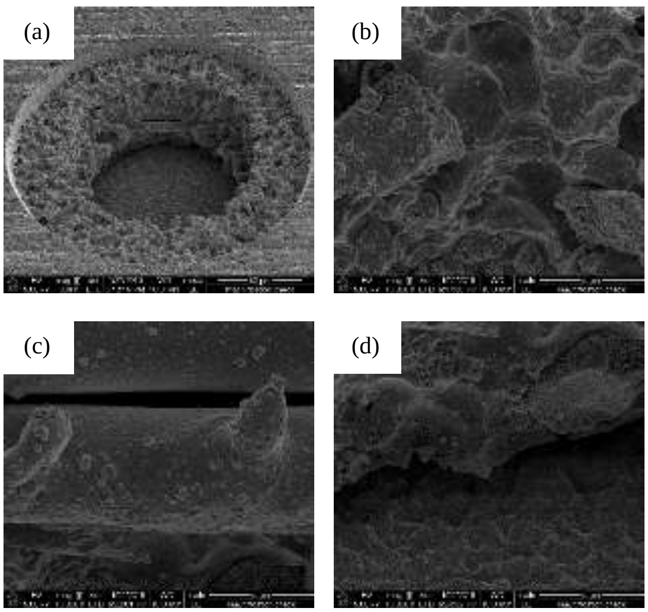
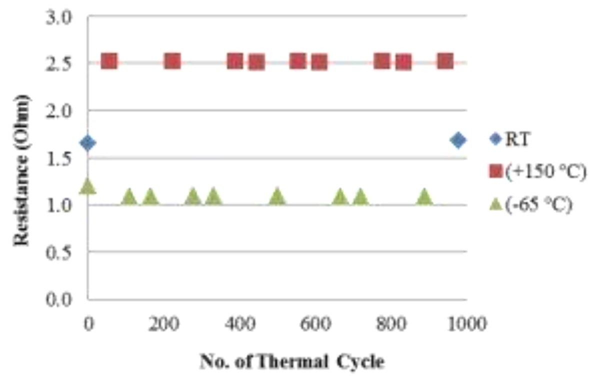


FIGURE 2. SEM IMAGES OF MICROVIAS AFTER ELECTROLESS COPPER PROCESS SHOWING FULL COPPER COVERAGE AND SMOOTH MORPHOLOGY. (A) TILTED OVERVIEW, 800X. (B) VIA TOP EPOXY, 10,000X. (C) TRANSVERSE GLASS, 10,000X. (D) VIA BOTTOM EPOXY, 10,000X.

Reliability Test: Liquid-to-Liquid Thermal Shock (LLTS)

Microvias allow signal and power transmission between the high density interconnect (HDI) layers of the printed circuit boards (PCB). One of the common methods to check the reliability of microvias is liquid-to-liquid thermal shock test. The acceleration mechanism for reliability is upon the coefficient of thermal expansion (CTE) of the device under test (DUT). Poor copper-plated microvias resulted in cracking and breaking in the plating caused by heat stress and mechanical stress. [2]

The specimen for testing was a glass epoxy substrate board (NPGN) with microvias of 100 um diameter. The sample was plated with Silver Catalyst MHC process, followed by acid duo and electroplating process. The sample was subjected to liquid-to-liquid thermal shock cycles from -65oC to 150oC using an ESPEC Thermal Shock Chamber TSE-11. The test was consisted of 1000 thermal shock cycles and each cycle lasted for 30 minutes. Changes in the conductor resistance of the substrate board were recorded. Traditionally a 10% increase in resistance of a circuit was considered a failure. From the results (Graph 3), the microvia has pass the LLTS with no significant change in conductor resistance was observed throughout the 1000 thermal cycles.



GRAPH 3. CHANGE IN CONDUCTOR RESISTANCE

The cross-section of the microvia was examined after the LLTS. No cracking or interconnect separation was observed under microscopic and SEM evaluation. (Figure 3 and 4) As a result, high reliability of the microvia is achieved with silver catalyst MHC process.

FIGURE 3. OPTICAL MICROSCOPE IMAGE OF MICROVIA CROSS-SECTION AFTER LLTS

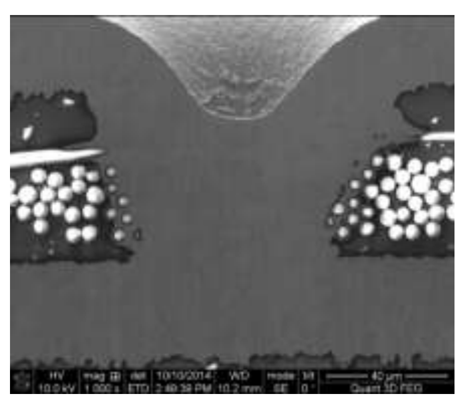


FIGURE 4. SEM IMAGES (1000X) OF MICROVIA CROSS-SECTION AFTER LLTS

CONCERNS ON SILVER MIGRATION

Silver migration may be defined as a process by which silver, when in contact with insulating materials under electrical potential, is moved in its ionic form from a metallic conductor either into or along the surface of an adjoining dielectric body. Such deposits of metallic silver lower dielectric strength and can ultimately cause dielectric failure. The problem of silver migration has long been recognized as a significant potential failure mode in many electrical and electronic systems.

The migration mechanism is influenced by the following factors:

- Temperature and moisture on the surface of dielectric material
- Voltage gradient and the distance between electrodes
- The presence of contamination

In particular, metallic silver on the conductor with the more positive applied potential (anode) is oxidized to a more soluble form. Dissolution of silver ions with presence of moisture and ionic contaminants will move under the influence of the electrical field toward the more negative conductor (cathode), where they are reduced back to silver metal.

Surface Migration Test

One of the greatest challenges of introducing silver catalyst for MHC process would be the concerns on silver migration. The risk of surface electrochemical migration has been evaluated according to standard method IPC-TM-650 2.6.14.1. The test board (IPC-B-25A) has been pretreated with MHC process applying silver catalyst (Sweller to Postdip steps) with 6-10 ug/cm^2 amount of silver catalyst adsorbed. (Figure5) The test board was electrically biased at 10V DC under an environment of 85 oC with 88.5% RH for 596 hours.

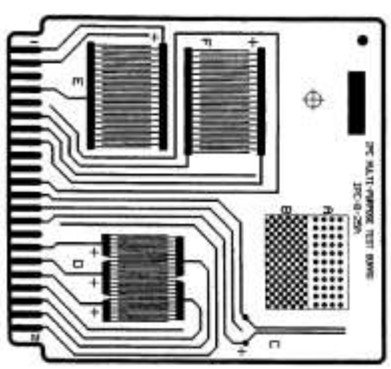
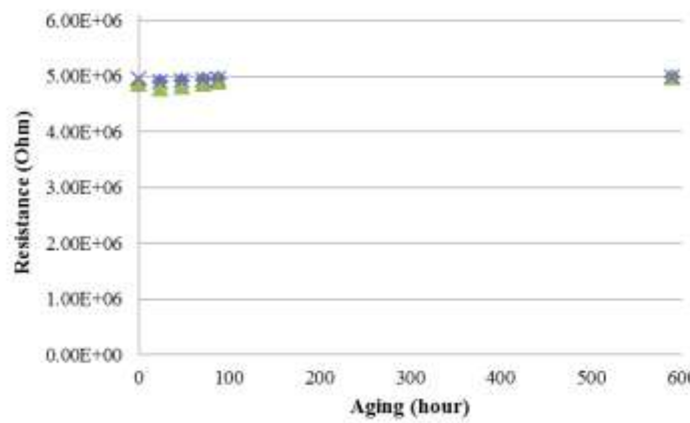


FIGURE 5. TEST BOARD DESIGN OF IPC-B-25A

After 596 hours of high temperature and high humidity aging, no significant resistance change was observed. (Graph 4) Despite of the fact that silver catalyst was adsorbed on the testing panel, no surface migration was detected according to the standard method.

The major differences between the general silver plating technology and silver catalyst for MHC process is that the silver catalyst comprises stabilizer system which could decrease the effect of electric current toward the silver catalyst. The stabilizers can maintain a steady environment around the silver catalyst and retard the oxidation to the ionic form. As a result, the risk of silver migration on silver catalyst is relatively low in comparable with other silver plating technology.



GRAPH 4. RESISTENCE CHANGE OVER 596 HOURS ELECTRICALLY BIASED

SUMMARY

Palladium-tin colloid and ionic palladium catalysts are widely applied in MHC process. As a novel catalyst, silver catalyst shows distinctive advantages on cost and reliability performance. From the results on deposition profile, microvia coverage and morphology, reliability study with liquid-to-liquid thermal shock, and the surface migration test, silver catalyst is a potential palladium substitution catalyst for MHC process.

REFERENCES

[1] Zhou, W.; Kwong, S.K.; Chan, C.Y.;Yee, K.W. A new MHC catalyst system - Nano-Silver, *Microsystems, Packaging, Assembly and Circuits Technology Conference (IMPACT), 2014 9th International* (**2014**)

[1] Freda, M.; Reid, P. Thermal Cycle Testing of PWBs - Methodology, *IPC Printed Circuit Expo, APEX & Designer Summit Proceedings* (**2009**)