CIRCUPOSIT™ 6530 Catalyst Process for Electroless Copper Metallization

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ABSTRACT

This paper describes the development of a new ionic palladium catalyst, CIRCUPOSIT™ 6530 Catalyst, along with a tartrate-based horizontal electroless copper bath, CIRCUPOSIT™ 6550, to meet the performance demands of high-density-interconnect (HDI) and packaging (PKG) substrates in horizontal electroless copper plating. Implementation of the new ionic catalyst process is demonstrated through excellent coverage and reliability performance of through holes and microvias on HDI and PKG substrates following processing in horizontal equipment, as well as peel strength on low profile dielectric materials in the semi-additive process. Results also showed that the new CIRCUPOSIT™ 6530 Catalyst demonstrated stable performance during customer qualification.

INTRODUCTION

The Pd/Sn colloidal catalyst has been commercially used for electroless metal deposition for decades. Yet its sensitivity to air leaves room for substitution.[1,2] In recent years, the packaging density of consumer electronic circuits has steadily increased along with the demands on increased reliability. Advanced boards, including high-density-interconnect (HDI) boards with microvias, are more frequently processed in horizontal mode. This is in part due to the more beneficial fluid dynamics allowing metallization chemicals to reach the bottom of microvias, especially in those microvias with a high aspect ratio. However, the increased solution agitation in the horizontal mode promotes Pd/Sn colloidal catalyst instability. Considerable efforts have been made to find new and more stable catalysts.[3-5]

The ionic palladium catalyst is intrinsically more air stable than the colloidal Pd/Sn catalyst because there are no air sensitive stannous compounds in the formulation and palladium is already in the 2+ oxidation state.[6] This feature makes the ionic catalyst ideal for horizontal processing of advanced boards. Once the ionic palladium catalyst particles adsorb onto the laminate surface and hole/via wall, a reducer step reduces the palladium ion to its metallic zero-valence state and renders the metal catalytically active for the initiation of electroless copper metallization.

This paper presents the development of a new ionic palladium catalyst, CIRCUPOSIT™ 6530 Catalyst,[1] which is being commercialized by Dow Electronic Materials to meet the reliability performance demands of HDI and PKG substrates in horizontal electroless copper plating. The CIRCUPOSIT™ 6530 Catalyst process has demonstrated excellent coverage and reliability performance in through holes and microvias on HDI and PKG substrates. Metallization of low profile dielectric materials for the semi-additive process has also been evaluated and good peel strength was obtained. Results showed that the new ionic catalyst was a robust system and the process demonstrated stable performance during the customer horizontal line qualification.

EXPERIMENTAL

CIRCUPOSIT™ 6530 Catalyst Preparation

The CIRCUPOSIT™ 6530 Catalyst was prepared by reacting palladium ions with an aqueous solution of a proprietary stabilizer. A buffer solution was added to maintain the catalyst pH at 9-10. The ionic catalyst solution is then ready for use as an activator for the electroless metallization. Optionally, the catalyst solution can be heated at 50 – 60 °C for a few hours before being applied as a catalyst. The ionic catalyst was characterized by ESI-MS, MALDI-MS, and NMR spectroscopy.

Sample Preparation

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All of the chemicals used for desmear, electroless, and electrolytic copper plating were standard Dow Electronic Materials products, except where otherwise noted. Specifically, a tartrate-based CIRCUPOSIT™ 6550 Electroless Copper bath designed for horizontal plating process was used for this qualification.

Six types of multilayer copper clad epoxy/glass laminates with 1 mm diameter holes designed by Dow Electronic Materials were used for routine backlight and interconnect defect (ICD) tests. The laminates include low-T_g, medium-T_g, high-T_g, and halogen/phosphorous free materials. Microvias of 100 µm diameter and 70 µm deep were used for routine pin-pull and high current tests (HCT).

For peel strength test, three kinds of dielectric materials were used. The surface roughness (Ra) ranged from 80 nm to 300 nm after desmear. After electroless copper plating, a 25 µm thick electrolytic copper was plated for peel strength measurement by an INSTRON 5564 Tensile Test machine. The peeling speed was 50 mm/min and the sample width was 10 mm.

CIRCUPOSIT™ 6530 Catalyst Adsorption

Bare epoxy/glass laminates were processed through the desmear to reducer steps. Palladium on the bare laminate surface was etched using aqua regia and solution Pd concentration was determined with a Varian SpectrAA 220FS atomic absorption spectrometer. The Pd surface adsorption was determined by dividing the amount of Pd by the surface area of the bare laminate.

CIRCUPOSIT™ 6530 Catalyst Aging Test

Accelerated aging and stability tests were conducted on the catalyst concentrates by placing samples in a 50 ℃ oven or a 4 ℃ refrigerator for 30 days. After that time, diluted catalyst working baths were prepared from the concentrates. The catalyst stability and plating performance were evaluated and compared with freshly prepared catalyst solutions as well as room temperature storage of the concentrates. Additionally, the catalyst working bath stability was evaluated during cycling tests.

Coverage and Morphology

Laminates with through-holes and microvias were processed through desmear to the electroless copper plating. The through-holes were routed from the test boards and cross-sectioned to the middle of the holes by manual grinding. The cross-sections from each panel were inspected on an Olympus GX 71 optical microscope with a light source behind the samples and backlight was graded on a scale of 0 – 5, with a rating of 4.5 being considered minimum acceptable coverage. A minimum of 10 holes were evaluated from each type of laminate. Microvias were cross-sectioned by a JEOL CP-09010 polisher and coverage in the microvias was obtained by SEM and FIB examinations using a Quanta 3D FEG 200 instrument. Copper deposit morphology was evaluated by optical microscope front light or SEM inspection.

Reliability Test

After electroless copper plating, laminates were plated with an acidic electrolytic copper, dried in an oven at 125 ℃ for 6 hours and solder shock tests were performed (6 x 10 sec at 288 ℃). The cross-sections of through holes/vias were examined for ICD under an optical microscope. For pin-pull test, the electroplated coupons were dried in an oven at 120 ℃ for 2 hours. The area around the vias was masked and the remaining surface copper was stripped off. The panels were subjected to solder float (5X) and a Cu pin was soldered to the remaining Cu pad on the panel surface. The copper pin was pulled by an elongation tester, Zwick Z2.5/TN1S. The break location within the plated via was then examined under an optical microscope. SEM was used to confirm the break location, if needed. For HCT test, a 2.3 Amp constant current, at no more than 11 V, was passed through the pattern and the laminate was observed under an IR camera. The circuit break time was recorded.

RESULTS AND DISCUSSION

CIRCUPOSIT™ 6530 Catalyst Adsorption

The ionic catalyst laminate surface adsorption depends on several factors including sweller, conditioner, laminate type, and catalyst solution pH. Dow Electronic Materials offers a variety of sweller and conditioner products for use with the ionic catalyst process. The catalyst solution pH should be controlled to maintain catalyst activity and optimize Pd adsorption onto the laminate surface. The optimal pH for the ionic catalyst working bath was determined by quantifying Pd epoxy surface adsorption and backlight performance. Figure 1 shows that pH 9 – 9.5 gave the highest Pd adsorption and BL ratings on the test laminates, and was selected as the CIRCUPOSIT™ 6530 Catalyst working bath pH.

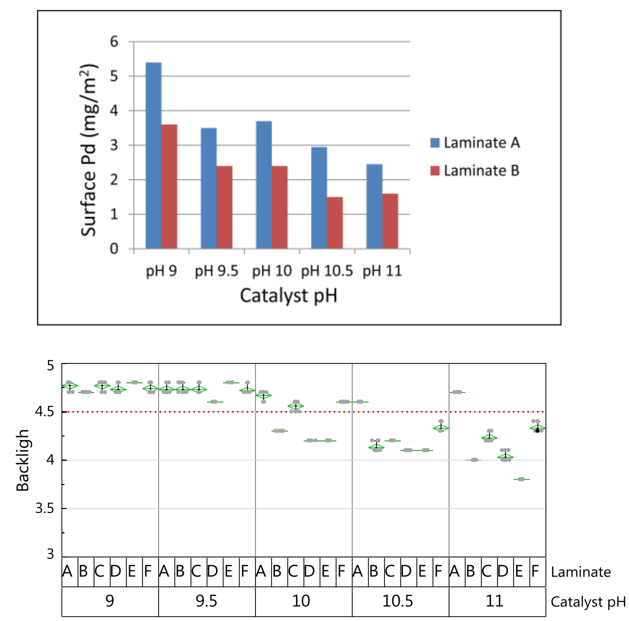

Figure 1: (Top) Palladium epoxy surface adsorption as a function of catalyst working bath pH. (Bottom) Catalyst working bath pH-dependent backlight ratings in beaker test.

Although ionic catalyst adsorption on the dielectric substrate is required for initiating electroless metallization and making the substrate conductive, catalyst adsorption on the innerlayer copper surface is not desired due to the contamination of the innerlayer surface and potential cause of ICDs. To confirm the selectivity of the ionic catalyst, similar Pd adsorption studies were conducted on Cu

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foils processed through the desmear to reducer process steps. The treated Cu foils were then etched and the etching solution was analyzed by ICP-MS for Pd. A Cu foil processed in the same manner as above except skipping the catalyst bath served as a blank control. Figure 2 indicates that there is no difference between the measured Pd adsorption of ionic catalyst treated samples and blank control samples. Further, after accelerated aging of the ionic catalyst bath (50 ℃ oven for 30 days) no change in Pd adsorption occurred. Also, the CIRCUPOSIT™ 6530 Catalyst samples each showed lower Pd adsorption as compared to traditional Pd/Sn colloidal catalysts.

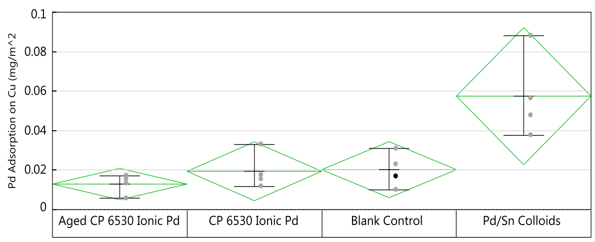

Figure 2. Pd adsorption of the CIRCUPOSIT™ 6530 Catalyst on the copper surface compared to the Pd/Sn colloids and blank copper film.

Reducer for CIRCUPOSIT™ 6530 Catalyst

A reducer step is generally required for ionic palladium catalysts, in which the palladium ions are reduced to metallic palladium, rendering them catalytically active for initiation of electroless copper plating. Many reducing agents have been reported for the reduction of Pd^{2+} in the literature. The prevailing reducing agent on the market for palladium reduction is dimethylamine borane (DMAB) based. However, due to its boron content, DMAB is not considered environmentally friendly.[7] Sodium hypophosphite was evaluated as a more environmentally friendly boron-free alternative. There was no difference in electroless copper coverage when comparing the two reducers in this test, suggesting that hypophosphite can be used as a DMAB replacement for this CIRCUPOSIT™ 6530 Catalyst.

CIRCUPOSIT™ 6530 Catalyst Stability

The CIRCUPOSIT™ 6530 Catalyst concentrate solution stability was evaluated in accelerated shelf life tests at 50 ℃ and 4 ℃. In both conditions, there was no cloudiness or precipitate formation observed after 30 days of aging. Working baths prepared from the aged catalyst concentrates had no deterioration or variation of backlight and ICD performance as compared with fresh catalyst solutions.

Stability of the ionic catalyst was further evaluated by cycling tests in horizontal application. The catalyst working bath was cycled to an approximate 10 m^2/L over a period of eight weeks. The aged catalyst bath remained active and backlight was above 4.5 after eight weeks of use. No cloudiness or precipitate formation was observed in the cycled catalyst bath. After cycling test, the catalyst working bath was analyzed by MALDI-MS and the spectrum was compared to the one obtained from a fresh catalyst working bath. There was no difference observed for the palladium species in the fresh and aged baths.

CIRCUPOSIT™ 6530 Catalyst Performance in Cycling

Throughout the catalyst cycling in the horizontal pilot line with the CIRCUPOSIT™ 6550 Electroless Copper bath, the ionic catalyst performance was continuously monitored. Except for the occasional replenishment to the catalyst working bath and pH adjustment, there was no additional maintenance required for the catalyst bath. Average backlight ratings for the through-holes was consistently above 4.5 for all six tested laminates (Figure 3); no ICD was found in the through-holes and microvias on the test laminates; an average of over 95% of pin-pull pass rate was obtained and the break time was over 60 seconds at 2.3 A for the HCT test. Figure 4 shows the images of plated blind microvia backlight coverage, zero ICD and no voids around the microvia bottom.

Both the shelf life and cycling tests demonstrate that the CIRCUPOSIT™ 6530 Catalyst is a robust catalyst that has a long bath life in horizontal process conditions.

CIRCUPOSIT™ 6530 Catalyst Performance in Customer Testing

The CIRCUPOSIT™ 6530 Catalyst and CIRCUPOSIT™ 6550 Electroless Copper process was evaluated in a customer horizontal production line, using both DOW's and the customer's test panels,

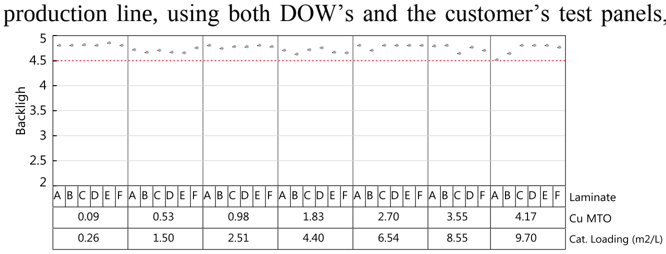

Figure 3. Average backlight rating for the six test laminates throughout the cycling test.

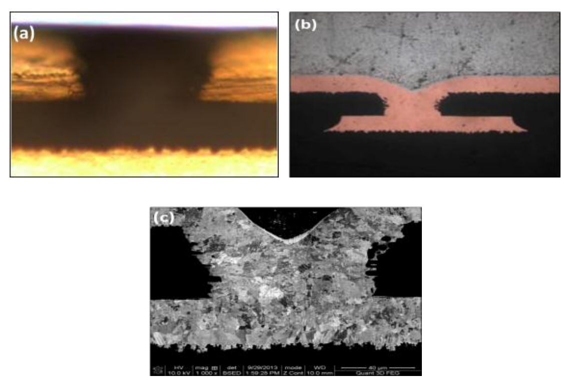

Figure 4. Images of the plated blind microvia showing (a) backlight coverage, (b) zero ICD, and (c) no voids around microvia bottom.

which included HDI and PKG substrates, and laminate materials such as bismaleimide-triazine (BT) resin. The process has passed customer qualification and is being used for mass production. Typical customer qualification test conditions and results are summarized in Table 1.

Board	Test Item	Conditions	Results
HDI	Hot oil shock test	260 ^{o}C 10 sec/20 ^{o}C 10 sec, 10 cycles	PASS
	Thermal shock cycling test	-55 ^{o}C 15 min/125 ^{o}C 15 min, 100 cycles	PASS
	IR reflow test	240 ^{o}C peak, 5 cycles	PASS

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PKG	Pressure cooker test	121 °C 100% R.H. 2 atm, 96 hrs	PASS
	Thermal shock cycling test	-55 °C 15 min/125 °C 15 min, 500 cycles	PASS
	HAST (Highly accelerated stress test)	85 °C 85% R.H., 168 hrs	PASS

Table 1. CIRCUPOSIT™ 6530 Catalyst and CIRCUPOSIT™ 6550 Electroless Copper customer qualification test conditions and results

In addition to the customer qualification items listed in Table 1, the CIRCUPOSIT™ 6530 Catalyst process was evaluated in the customer horizontal line for backlight, electroless copper deposition rate, morphology, ICD, pin-pull, and HCT performance. Satisfactory results were obtained for these test items on customer's test boards. The CIRCUPOSIT™ 6530 Catalyst and the CIRCUPOSIT™ 6550 Electroless Copper baths were stable and no performance decay was observed for at least three weeks of testing in the customer's line. Figure 5 shows the SEM images of deposited copper on microvias.

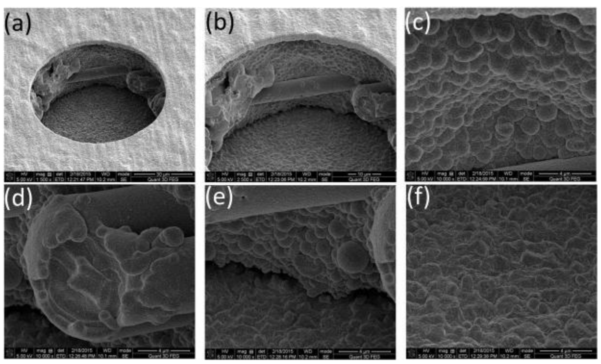

Figure 6. SEM photos showing morphologies of copper deposit from the CIRCUPOSIT™ 6530 Catalyst and CIRCUPOSIT™ 6550 Electroless Copper process. (a & b) Overview of a microvia, (a) × 1,500, (b) × 2,500. (c) Via top resin, × 10,000. (d) Glass, × 10,000. (e) Via bottom resin, × 10,000. (f) Via Cu pad, × 10,000.

CIRCUPOSIT™ 6530 Catalyst for SAP

Integrated circuit package substrates are generally plated by semi-additive process (SAP), in which high peel strength on low surface profile material, uniform deposition in microvia holes and high Cu-Cu joint reliability are required. The CIRCUPOSIT™ 6530 Catalyst was tested in the SAP with a specially formulated SAP electroless copper bath CIRCUPOSIT™ ADV 8550 Electroless Copper, available from Dow Electronic Materials.

Although the smooth dielectric surface makes achieving high adhesion of the deposited copper on the surface difficult, the CIRCUPOSIT™ 6530 Catalyst showed excellent and stable peel strength on the dielectric materials. Figure 6 indicates the resulting peel strength on major dielectric materials for IC package.

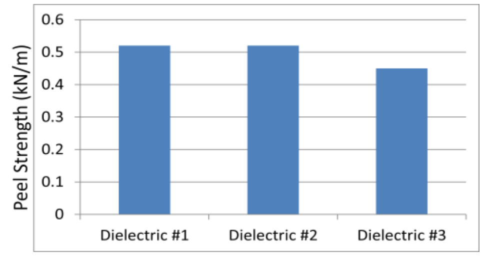

Figure 6. Peel strength obtained using CIRCUPOSIT™ 6530 Catalyst on various dielectrics in the SAP.

The uniformity of the copper deposition on the dielectric surface and inside the microvia is also important for fine pattern design in the IC substrate. The CIRCUPOSIT™ 6530 Catalyst had high deposition uniformity on the dielectric surface and inside the microvia, in which a throwing power of 75% was obtained, as shown in Figure 7. The figure also shows that the dielectric near the microvia bottom was fully covered by electroless copper.

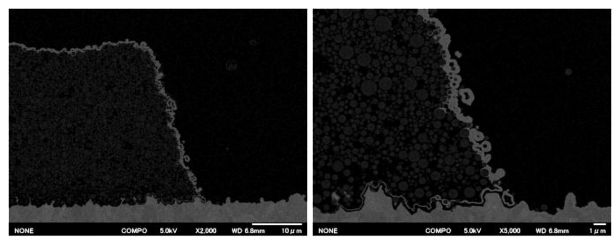

Figure 7. Images of uniform deposition inside microvia (50 µm × 35 µm) on low profile substrates in the SAP. (L) one side of whole via, × 2,000. (R) one side of via bottom, × 5,000.

Conclusion

A new CIRCUPOSIT™ 6530 Catalyst has been formulated and optimized for HDI and PKG laminates for horizontal process equipment, along with a tartrate-based horizontal CIRCUPOSIT™ 6550 Electroless Copper. The process has been qualified in a customer's horizontal plating line, providing excellent and stable performance on backlight, ICD, pin-pull, HCT, copper deposit thickness and morphology. In addition, high peel strength was obtained with the new CIRCUPOSIT™ 6530 Catalyst on major dielectric materials in the semi-additive process. The new ionic catalyst system is being commercialized at a number of customers.

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