

Three Methods for Pcb Via Metallization – Investigation and Discussion

Svetozar ANDREEV*, Slavka TZANOVA* and Nina SPASOVA*

*Technical University of Sofia, Department of Microelectronics, 1000, Sofia, Bulgaria,

E-mail: svetozar_a@tu-sofia.bg

Abstract – The present paper describes the results, obtained during the investigation of three chemical methods for multilayer Printed Circuit Board (PCB) via metallization. All these methods have one and the same purpose – to provide metal (copper) deposition on the dielectric surface inside the PCB vias and make electrical connection between the separate layers. However, they have different chemical composition and respectively price, process complexity, possibility to treat different PCB materials. In this paper the metallization quality of each method is investigated, depending on the type of the PCB material, the via hole size, the material thickness and the via location on the test substrate

Keywords – Dielectric activation, Metallization, Printed Circuit Board, Via

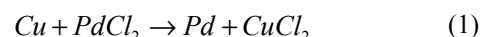
I. INTRODUCTION

When we talk about the Printed Circuit Board (PCB) technology, it is clear that the via metallization is one of the most important techniques in the PCB manufacturing process. The technique relates to the deposition of copper film on the dielectric surface inside the drilled holes in the PCB material, named vias. For this purpose chemical methods are used and have been successfully applied in the PCB industry for over 40 years. They differ on chemical composition, process sequence, chemical stability and feasibility. Basically, these methods consist of three major steps – dielectric surface activation, chemical electro-less copper seed layer deposition and subsequent electrochemical thickening of the copper seed layer. The first step is critical, because the whole metallization process depends on the good activation of the dielectric surface.

In general, the electroless copper plating process is a very effective method for copper coatings on a non-conductor surface. It has been known for more than a century, but in the last 3 – 4 decades was ameliorated and obtained large scale applications, especially in the PCB industry. As mentioned above, the key in this process is the dielectric surface activation. The classical way to perform this step is the surface treatment in solution, containing stannous salts (sensitization), followed by treatment in another solution, which contains precious metal salts (ordinarily palladium). The purpose of sensitization is the deposition on the dielectric surface of a film of 2nd valence stannous ions, which act subsequently as reducers for the palladium ions, reducing the metal ions to the metallic state. This reduction takes place at the solid/liquid catalytic interface.

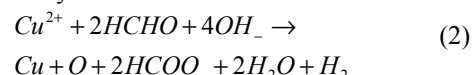
The electroless copper plating process, however, has some disadvantages, which cannot be neglected. Firstly, the

electroless bath containing copper ions and reductant agent is unstable and has low durability. Secondly, when processing the vias of a multilayer PCBs, which are a system of alternating “copper foil-dielectric-copper foil-dielectric” layers, a contact exchange reaction occurs on the foil:



This reaction is undesirable, since the palladium, released at the ends of the copper contact pads, prevents the good adhesion of the copper foil with the chemically deposited copper layer. In addition, the solution is rapidly depleted, and the losses of precious metal are increasing.

One more disadvantage in the case of electroless metallization is that, besides the copper deposition, hydrogen is inevitably released:



The liberated hydrogen clogs the vias, preventing the completion of the process.

Considering this, researches have been conducted and efforts have been spent, aiming to discover better methods for dielectric chemical metallization. These methods can make the electro-deposition of copper possible without the need of preliminary conductive copper film, deposited via electroless copper. Therefore they are called direct copper plating methods and the dielectric activation is named direct activation. Chi-Chao Wan in his work [1] has described the most effective and applicable of these methods with their advantages and disadvantages, grouping them in three types – Palladium colloidal system, Carbon colloidal system and Conductive polymer system. The Palladium colloidal activation system is similar to the traditional electroless copper plating process, as the activator used is again Pd/Sn. The difference comes in the replacement of the electroless copper with a promotion step. Since the carbon is conductive, metallization processes, based on this system, have been developed and successfully implemented in the PCB industry.

Another relatively new method for direct metallization is based on solutions, containing unstable copper salts [2]. Activating solutions, whose action is based on the reaction of thermal decomposition of copper hypophosphite, are used to metallize the PCB vias as well.

The direct metallization methods are considered to be more stable, simple and able to eliminate some of the disadvantages of the classical electro-less copper deposition. A brief comparison between the two types is given in table 1.

TABLE 1. COMPARISON BETWEEN ELECTRO-LESS AND DIRECT METALLIZATION

Parameter	Electroless copper plating	Direct copper plating
Process stages	Activation + electroless deposition	Activation
Deposited layer density	Friable	Dense
Presence of a barrier layer between the galvanic metallization of the via and the contact pads ends on the inner layers	Yes	No
Hydrogen release	Yes	No
Solution viscosity	Viscous	Less viscous
Process control	By 5 parameters	By 2 parameters

In the present paper three methods for PCB via metallization were investigated. Test substrates with different via diameter were prepared and metalized. The obtained results were observed by means of polished sections across the vias.

II. EXPERIMENTAL

A. Chemistry

The first chemical solution, chosen for the investigations in the present work, is the well known palladium activation system [3,4,5,6]. In order to be metalized, the dielectric surface is treated in such solution in several steps including Degreasing, Micro-etching, Oxide removing, Activation “Pre dip” bath, Activation bath, Post activator bath, followed by electroless copper deposition. The last process step will deposit a thin layer of copper (0.5 – 1 μm) and we can continue the deposition by galvanic way.

The second dielectric activating solution is carbon-based [5]. The experiments were conducted with Activator 310 from “LPKF Laser & Electronics AG”. The activator is comprised of a water solution of carbon particles and organic binders with potential of hydrogen (pH) in the range from 9,6 to 10,4 (alkaline features). To achieve electro-conducting features, the activator is treated in the following manner: 1.) the test substrate is dipped in the activator solution for 15 minutes, followed by 2.) drying and stabilization at 60°C for 15 minutes. A black conductive layer of carbon is formed and direct electroplating can be applied.

Third activating solution was used for the investigations. It is composed of Copper hypophosphite, Ammonium hydroxide and wetting agent. The Copper hypophosphite has low thermal stability. The thermal decomposition (thermolysis) of this salt is an oxidation-reduction process in a solid phase with the formation of metallic copper, copper hydride, copper (I) oxide. The decomposition

temperature is 50 °C, the process proceeds at a very high velocity and is practically uncontrollable. To control the decomposition process, solvate groups are introduced into the salt molecule. For this, copper hypophosphite is dissolved in a 25% solution of ammonia. After the standard treatment, the test substrates are immersed in the such obtained activator of the complex salt at room temperature for 2-3 minutes, left in air for 3-7 minutes, and then heated with air circulation at 130-145 °C for 15-20 minutes. When heated, crystallization of the salt first takes place, followed by the deposition of copper. The completeness of thermolysis is checked visually, according to the color of the precipitate formed. The color in the vias should be from dark brown to black. Then, jet flushing with running water is carried out and the substrate is ready for subsequent electrochemical copper deposition.

B. Test samples preparation

In order to investigate the dielectric activation capability of the three chemical methods, cited above, test samples were prepared and their topology is shown in figure 1. The samples are 5x5 cm. large and have different thickness of the dielectric core. In this work 0.5 Oz two-sided FR4 with 0.80 mm dielectric thickness, 0.5 Oz two-sided FR4 with 1.5 mm dielectric thickness and 0.5 Oz two-sided Rogers 4003 [7] with 0.508 mm dielectric thickness were used. While the FR4 dielectric core has an epoxy/glass composition, the Rogers core is hydrocarbon-ceramic based. As it can be seen on the figure, the vias drilled in the test samples consist of 5 groups by 5 holes with 0.2, 0.4, 0.6, 0.8 and 1 mm diameter respectively, situated at the upper and lower corners and the center of the substrate. The test samples project topology was designed in the Altium Designer 13 CAD system, and for the vias drilling LPKF ProtoMat S103 machine was used.

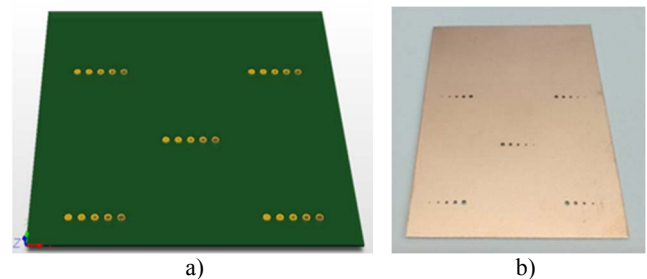


Figure 1. Test sample topology: a) project topology; b) FR4 test sample

After the activation process all the samples were subjected to electrochemical copper deposition in an acid electrolyte bath, containing Copper sulfate – 80 g/l, Sulfuric acid – 100 ml/l, Chlorides – 50 mg/l, Shining agent – 6 ml/l. The electro-deposition of copper was performed by way of a moving front mechanism for 60 min at room temperature.

III. RESULTS

For the purposes of investigation polished sections were made across the metalized vias, as shown in figure 2. By means of a microscope MIK 4 the deposited copper

uniformity inside the vias was observed and the copper thickness was measured.

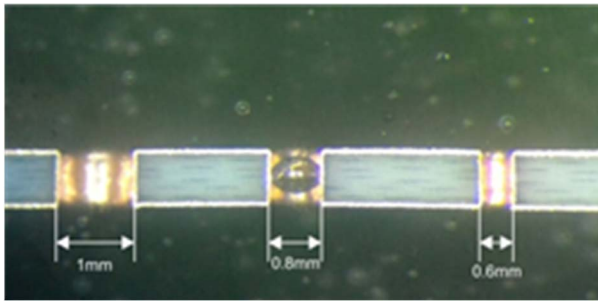


Figure 2. Polished section of 0.8 FR4 with 1 mm, 0.8 mm and 0.6 mm via diameter

The measured vias copper thickness of the test samples is presented in tables 2, 3 and 4. Table 2 gives the thickness values of the samples, treated in the classical Palladium activation system, table 3 shows the values of Carbon activated samples and table 3 – of samples with Copper hypophosphite activation.

TABLE 2. VIA COPPER THICKNESS OF TEST SAMPLES WITH PALLADIUM ACTIVATION

Base material	RO4003	FR4 0.8	FR4 1.5
Via diameter, mm	Via copper thickness, μm		
1	22 - 24	24 - 26	16 - 18
0.8	22 - 24	24 - 26	16 - 18
0.6	22 - 24	24 - 26	16 - 18
0.4	22 - 24	24 - 26	16 - 18
0.2	22 - 24	24 - 26	16 - 18

TABLE 3. VIA COPPER THICKNESS OF TEST SAMPLES WITH CARBON ACTIVATION

Base material	RO4003	FR4 0.8	FR4 1.5
Via diameter, mm	Via copper thickness, μm		
1	20 - 22	16 - 18	14 - 16
0.8	20 - 22	16 - 18	14 - 16
0.6	20 - 22	16 - 18	14 - 16
0.4	20 - 22	16 - 18	14 - 16
0.2	20 - 22	16 - 18	14 - 16

TABLE 4. VIA COPPER THICKNESS OF TEST SAMPLES WITH COPPER HYPOPHOSPHITE ACTIVATION

Base material	RO4003	FR4 0.8	FR4 1.5
Via diameter, mm	Via copper thickness, μm		
1	20 - 22	16 - 18	12 - 14
0.8	20 - 22	16 - 18	12 - 14
0.6	20 - 22	16 - 18	12 - 14
0.4	20 - 22	16 - 18	12 - 14
0.2	20 - 22	16 - 18	12 - 14

It can be seen that the thicker via metallization was obtained with the Palladium activation system, which includes electro-less copper deposition. This is the reason

for the difference of 2 to 6 μm in the via copper thickness, compared with the other two methods.

IV. CONCLUSION

All the three chemical methods for dielectric surface metallization inside the PCB via demonstrated good results with all PCB material types. The deposited copper layer, observed through the via polished sections, was uniform and shine. It was found that the copper thickness inside the vias does not depend on the via diameter for a single test sample. However, the samples with larger dielectric core thickness demonstrated smaller via copper thickness.

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