Novel formaldehyde-free electroless copper for plating on next-generation substrates

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Abstract

This work describes a new type of formaldehyde-free electroless copper electrolyte that can be used for a broad set of applications and materials, especially for the processing of next-generation substrates. The plating solution was successfully applied in both, a laboratory and production-scale environment. The results have been evaluated in detail and were benchmarked against a formaldehyde-based reference. A characterization of the obtained metal films was carried out by different analytical techniques, including microscopy, X-ray fluorescence (XRF), scanning electron microscopy (SEM), adhesion tests and non-blister verification. Additionally, studies concerning chemical bath stability, throwing power and electrical reliability have been made. Based on the obtained data we believe that the current achievements represent a suitable technology to replace formaldehyde in existing printed circuit board (PCB) production without loss of process performance and thus provide a sustainable "green" alternative to the industry.

Key words

Electroless Copper Plating, Formaldehyde-Free, Printed Circuit Board (PCB), Plating Through Hole (PTH)

I. Introduction

The electroless deposition of metal and metal alloys is a widely applied technique in general metal finishing and in the production of electronics materials. Especially the electroless deposition of copper is widely used due to its relatively low process cost, easy maintenance and the good electrical conductivity of the obtained layers, which allows a subsequent build-up by galvanic metal plating.
Due to their challenging technical requirements [1] the highest performance standards are required for the electroless copper solutions applied during the production of semiconductors or PCBs. The processes have to achieve excellent substrate coverage with metal, provide coatings with high conductivity and uniformity and should lead to reliability results fulfilling current industry standards (e.g. copper to copper adhesion). Moreover, the solution has to deposit a copper layer in such a way that delamination failures are avoided on all types of dielectrics.

An electroless copper plating bath generally consists of a copper(II) salt, one or more complexing agents, pH adjustment by caustic or a buffer system, one or more reducing agents, and different inorganic or organic additives [2]. These additives function as deposition moderators and stabilizers, as well as prevent the uncontrolled copper reduction in the thermodynamic instable solution. Additionally, they have a significant impact on deposition speed, the morphology of the deposited crystals and on the intrinsic properties of the final metal layer [3].

The reducing agent formaldehyde is today's dominating substance in industrial electroless copper processes. The aldehyde has the advantage that it is inexpensive, provides a strong reduction potential in alkaline aqueous solutions and generally leads to copper deposits of high quality. It has successfully been used in combination with various complexing agents, such as EDTA [4], triethanolamine (TEA) [4], quadrol [5], tartrate [6], citrate [7], different carbohydrates and carbohydrate derivatives [8].
Unfortunately, formaldehyde is a known danger to human health and the IARC (WHO International Agency for Research on Cancer) has classified the substance as a human carcinogen [9]. The high volatility of formaldehyde generally increases the exposure to the hazard so much that

critical air concentrations can easily be exceeded. Having these threads in mind it is obvious that the development of non-toxic electroless copper plating solutions has become essential today. Different bath formulations based on alternative reducing agents, including hypophosphite [10]-[11], dimethylamine borane [12], glyoxylic acid [13] or 2,2´-dialkoxyacetaldehydes [14] are reported in literature. Nevertheless, none of the so far developed electrolytes has succeeded to replace existing formaldehyde-based processes until now due to high industrial standards in terms of cost-efficiency, process stability and performance. The introduction of more sophisticated production technologies and materials has even increased the difficulty to replace standard formaldehyde-based processes because of the high knowledge and experience base that is available for these long established products.

In recent years, the PCB industry has shifted its interest more and more towards very smooth substrate materials with low coefficients of thermal expansion. The materials allow a further miniaturization of circuits and are optimal for the electrical integration of semiconductor units (IC substrates). To reach the smallest lines and spaces, the electroless copper deposition is typically carried out on the bare resin surface followed by application of a patterned dry film and galvanic copper plating (semi-additive process, SAP). Unfortunately, the smooth substrate topography leads typically to a limited adhesion of the electroless copper layer, which increases the risk of delamination and blister formation. To prevent this, the intrinsic physical properties of the metal film (and therefore the chemical properties of the copper bath) are critical [15]. A key factor is that the metal deposition occurs under the generation of internal tensile stress so that the blister tendency is minimized. Formaldehyde-based plating solutions could successfully be modified to meet this requirement by the co-deposition of nickel which allows the adjustment of internal stress. Nevertheless, very little knowledge is available regarding chemical approaches that can be applied when alternative reducing agents are used. The exchange of the reducing agent generally requires the complete redesign of the electroless system, including the correct choice of complexing agents and additives, the readjustment of chemical concentrations and the optimization of physical working parameters.

II. Results

To be able to fulfill all industry requirements for a modern electroless copper plating solution, the correct combination of suitable reducing agents, complexing agents and additives is essential. The best values in terms of performance were obtained for a combination of glyoxylic acid as the reducing agent with a biodegradable organic complexing agent that also allowed the co-deposition of nickel. The incorporation of nickel in the deposit was the

most effective way to induce tensile stress in the layer and avoid blistering on ultra-smooth materials. The addition of certain organic additives finally led to a stable electroless copper bath with a constant deposition speed and metal layers with defined morphology. The bath stability could be maintained by the usage of stabilizing agents. The developed formulation led to the new product named Ecoganth® MV G2.

Fig. 1 describes the obtained copper layer thickness after plating for varying times on a smooth dielectric. The conventional formaldehyde-based copper bath Printoganth® MV TP1 was used as the reference system. It represents a mass-production proven high-performance bath for SAP technology. Layer thicknesses were determined by SEM after opening of the Cu film by focused ion beam (FIB). The data shows that the plating speed is a bit slower for Ecoganth® MV G2 which leads to slightly increased immersion times for a desired layer thickness. The deposition led in both cases to void- and defect-free salmon-pink metal films.
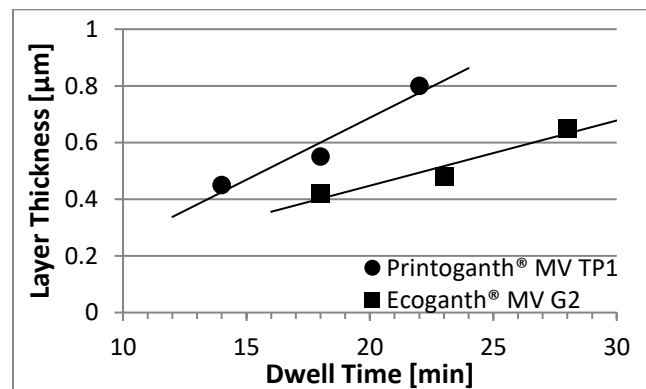

Figure 1: Copper deposition on a dielectric (next-gen A) with varying plating times. As electroless copper plating solutions, Printoganth® MV TP1 and Ecoganth® MV G2 were used. The layer thickness was determined by SEM/FIB.

The long-time performance of Ecoganth® MV G2 was studied by its usage over a period of several days. To investigate the plating performance during ageing of the bath, layer thicknesses were determined by XRF on acrylonitrile butadiene styrene (ABS) and on FR4 material. The obtained thickness values differ for both materials due to a different surface roughness. The immersion time was in each case 30 minutes. Fig. 2 shows that the copper deposition speed remains constant even after significant throughput. At the end of the experiment the total copper makeup content has been replenished more than three times without the occurrence of coverage issues.

Another critical performance factor that benchmarks an electroless copper bath is the plating efficiency in through-holes. The presence of exposed glass fibers in the holes

requires continuous plating not only on resin, but also on the glass. Coverage issues can potentially lead to connectivity problems and voids. The backlight test was introduced as an industrial standard test to investigate the coverage of the through-hole sidewalls with metal. A value of D10 represents a perfect coverage, whereas a D0 represents zero coverage. D8 or a better result is typically required in industry. Fig. 3 summarizes backlight results for a set of materials obtained after plating with Ecoganth® MV G2 and with the reference system Printoganth® MV TP1. The graph shows that excellent through-hole plating was achieved with both plating solutions.
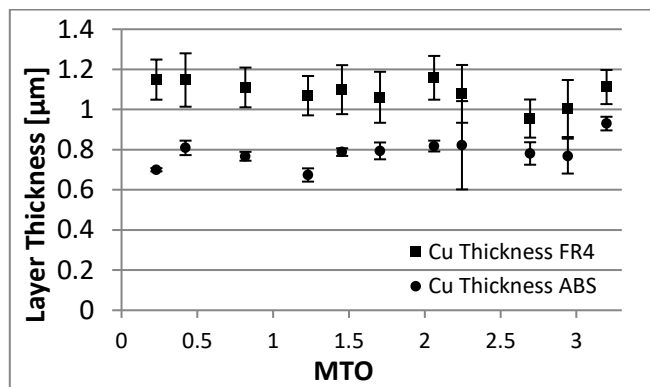

Figure 2: Copper deposition on FR4 and ABS material with increasing bath age using Ecoganth® MV G2. The plating time was in each case 30 minutes. One MTO (metal turnover) describes the complete exchange of the makeup copper content by replenishment.
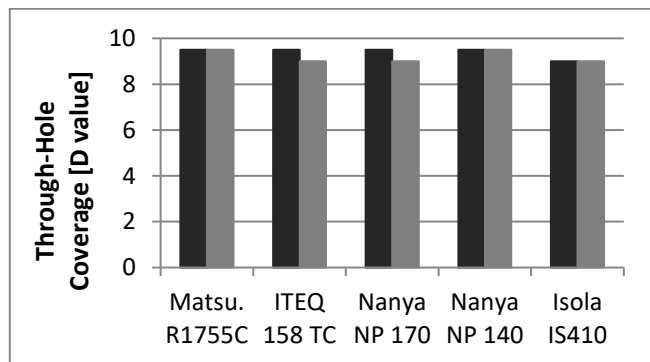

Figure 3: Through-hole coverage for different materials after plating with Printoganth® MV TP1 (black) or Ecoganth ® MV G2 (grey).

Delamination by blistering is a common problem that can occur on smooth PCB materials. A well-known way to suppress the formation of blisters is the induction of tensile stress in the metal layer during its formation, typically by the co-deposition of nickel. Ecoganth® MV G2 deposits about 1 – 2 % nickel in the layer, depending on the surface topography (0.5 – 1 % for Printoganth® MV TP1). The blister tendency of the deposits prepared by the two copper baths was investigated by plating tests on smooth PCB

materials. The prepared layers had a thickness of 0.5±0.1 µm (absolute) measured by SEM/FIB. The layer morphology of the deposits is shown in Fig.4 on GXT31 as an example. Table I summarizes the results of the adhesion experiments. In none of the tests blisters were observed, even for substrate B with a root mean square roughness of only 55 nm (SQ).
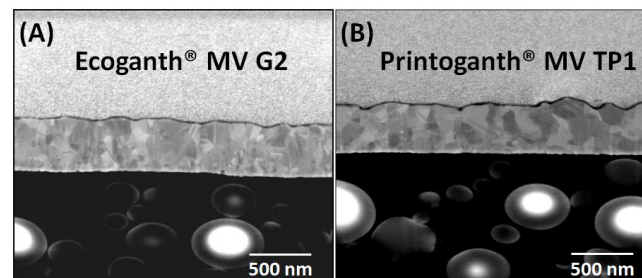

Figure 4: SEM images of layers prepared by (A) Ecoganth® MV G2 and (B) Printoganth® MV TP1 on GTX31.

Table I: The blistering tendency on different materials was studied for the plating baths Printoganth® MV TP1 and Ecoganth® MV G2. Layer thicknesses are absolute values determined by FIB-cut/SEM. Roughness values are given as root mean square roughness (SQ) and average roughness (SA). The formation of blisters was observed in no case.

Material	Rough-ness		Printoganth MV TP1	Ecoganth MV G2
	SQ [nm]	SA [nm]	[Cu thickness [µm] / blister]	[Cu thickness / blister]
GX92	192	137	0.54 / no	0.41 µm / no
GXT31	97	66	0.53 µm / no	0.53 µm / no
Next-gen A	121	102	0.45 / no	0.51 µm / no
Next-gen B	55	39	0.58 µm / no	0.51 mm / no

Besides the internal stress that is present in a copper layer, adhesion is a key factor that determines the blistering tendency. Peel strength and LUMiFrac® measurements were carried out to benchmark the adhesion of Ecoganth® MV G2 films on different substrates against the reference Printoganth® MV TP1 (see experimental section for more details). The results of the investigations are shown in Fig. 5. The peel-strength values obtained for three tested materials (Fig. 5A) correlate with their roughness values (Table I). On the other hand, the peel strength values do not differ significantly for the two tested electroless plating solutions. In summary, the data show that films prepared by Ecoganth® MV G2 have a very similar substrate adhesion compared to those prepared by Printoganth® MV TP1. This statement is further supported by LUMiFrac® investigations on an ultra-smooth PCB material (Fig. 5B) where the required force to remove the copper layer from the substrate surface was about 6 MPa for both plating baths.
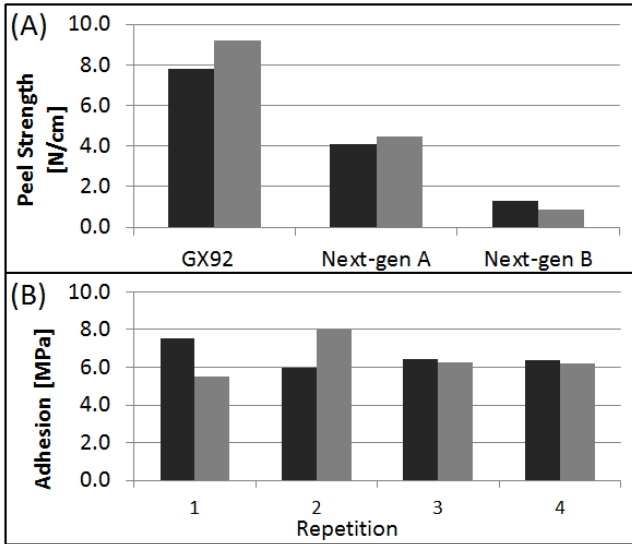
Figure 5: Adhesion on smooth PCB materials. (A) Peel strength values observed for GX92 and two next-gen materials after plating with Printoganth® MV TP1 (black) or Ecoganth® MV G2 (grey). The obtained values are similar. (B) LUMiFrac® adhesion test results on a next-gen material (next-gen B) after plating with Printoganth ® MV TP1 (black) or Ecoganth ® MV G2 (grey). The obtained adhesion values are similar.

Further detailed studies were carried out concerning the electrical reliability achieved by the formaldehyde-free copper bath. The solder shock test is a commonly applied thermal stress test that investigates the strength of the copper to copper interconnections in PCBs. A standard test procedure based on six shocking cycles at a temperature of 288°C was applied [16]. The results of the tests are shown in table II. Nine test coupons with 320 interconnections were processed. The total number of interconnections was 2880. No interconnection defects (ICDs) were found. The absence of defects at the given test conditions indicates a similar performance as observed for Printoganth® MV TP1 (data not shown).

Table II: Solder shock test results for Ecoganth® MV G2. The substrates were shocked by floating six times (three times per side) on liquid tin/lead (288 °C) for 10 seconds. No interconnection defects were observed.

Cu bath	Shocking conditions	Coupon #	Inter-connections	ICDs
Ecoganth® MV G2	6 x 288 °C	1	320	0
	6 x 288 °C	2	320	0
	6 x 288 °C	3	320	0
	6 x 288 °C	4	320	0
	6 x 288 °C	5	320	0
	6 x 288 °C	6	320	0
	6 x 288 °C	7	320	0
	6 x 288 °C	8	320	0
	6 x 288 °C	9	320	0

The reliability performance was also studied by the processing of daisy chain test boards. Each panel had a total number of 517440 blind microvias (BMVs). Two panels were used for each type of copper bath, resulting in a total number of 1034880 BMVs per tests. No defects were found for Ecoganth® MV G2 and Printoganth® MV TP1 (table III).

Table III: Daisy chain results obtained for Ecoganth® MV G2 and Printoganth® MV TP1. 517440 blind microvias (BMVs) were investigated per panel resulting in a total amount of 1034880 examined vias per electrolyte. No failures were observed in any of the plating experiments.

Bath	Panel	BMVs	Failures
Ecoganth® MV G2	1	517440	0
	2	517440	0
Printoganth® MV TP1	1	517440	0
	2	517440	0

Finally, the throwing power performance of the two electroless copper products was compared. Samples with blind microvias were plated in the two solutions and subsequently thicknesses of the deposited films were evaluated by SEM. The vias had a dimension of about 30 x 25 µm. The results of the experiments are shown in Fig. 6. The relative copper distribution in layers prepared by Printoganth® MV TP1 was excellent and the results achieved by Ecoganth® MV G2 were significantly above standard. Voids were not observed in any of the experiments.

$$TPBE = \frac{(B1 + B2)}{(E1 + E2)}$$

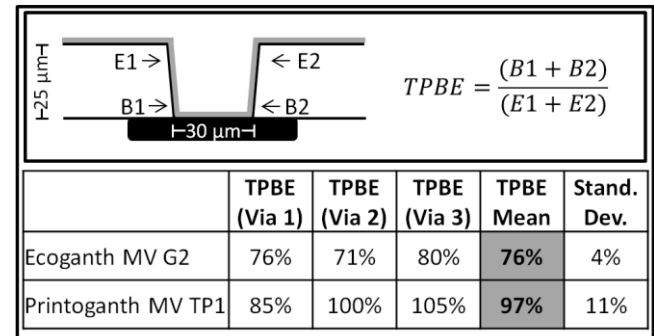|	TPBE (Via 1)	TPBE (Via 2)	TPBE (Via 3)	TPBE Mean	Stand. Dev.
Ecoganth MV G2	76%	71%	80%	**76%**	4%
Printoganth MV TP1	85%	100%	105%	**97%**	11%

Figure 6: Throwing power (TPBE) observed after electroless copper plating using Printoganth® MV TP1 and Ecoganth® MV G2 on a next-gen material (next-gen A). The dimensions of the investigated BMVs were about 30 µm x 25 µm (b x h).

III. Experimental Section

A. Materials

The used process chemistry is commercially available from Atotech. Substrate materials are also commercially available and were purchased from different suppliers. The materials were manufactured by the ITEQ Corporation, the

Isola Group, the Nan Ya Plastics Corporation, the Panasonic Corporation and Ajinomoto Co. Inc. The next-gen substrates are not commercially available due to their development stage. ABS coupons (30 mm diameter, 1.25 mm thickness) were purchased from Metak GmbH (Burgwald, Germany).

Backlight test coupons (50 mm x 50 mm) contained evaluation holes with a diameter of 1 mm. Solder shock tests coupons (50 mm x 50 mm) consisted of the material IS410 and contained 4 copper inner layers. The hole size was also 1 mm. Daisy Chain test boards contained the resin R1755C/R1650M. The BMV dimensions were 100 x 65 µm (b x h). 42 x 44 = 1848 BMVs were forming one daisy chain. A number of 280 grids was present on each board (140 grids per side), resulting in a total number of 517440 BMVs per panel.

B. Pretreatment and Activation of Substrates

Desmear: Test panels and coupons for investigations on the deposition rate, backlight performance, electrical reliability (solder shock test, the daisy-chain test) and throwing power were desmeared before usage. Desmear was carried out using an industrial permanganate-based process consisting of i) a resin swelling step, ii) an etch step and iii) a reduction step (removal of MnO_2). Washing of the samples by water was carried out after each step. The substrates next-gen A and B were used without desmear. The process conditions are summarized in table IV.

Table IV: Desmear conditions. The immersion times are used for all substrates, excluding GX92 and GXT31. In the case of these two substrates, all three immersion times were doubled (10, 20, 10 min).

Process	Temp	Time
Securiganth® MV Sweller	70 °C	5 min
Securiganth® MV P-Etch	80 °C	10 min
Securiganth® MV Reduction Conditioner	50 °C	5 min

Substrate Cleaning and Activation: Before the actual activation, all substrates were intensively cleaned. To this end, the samples were immersed into an alkaline cleaner, washed with water and subsequently treated by a sodium peroxodisulfate-based etch solution to remove about 1 µm of surface-exposed copper. The immersion time was adjusted accordingly (table V). The substrates were again washed using water. Subsequently, the samples were treated with a Pre Dip solution that contained wetting agents and then were directly transferred into an ionogenic Pd-activator. After an adsorption period of 4 minutes, the samples were washed with water and immersed into a dimethylaminoborane (DMAB)-containing reduction solution. During this step, Pd(0) seeds are created on the surface. Finally, the substrates were rinsed with water and

immersed into an electroless plating electrolyte. The cleaning and activation conditions are summarized in table V.

Table V: Cleaning and Activation

Process	Temp	Time
Securiganth® MV Cleaner PF	60 °C	4 min
or Securiganth® MV Cleaner GFR	60 °C	4 min
Securiganth® MV Etch Cleaner SPS	35 °C	Adjusted
Neoganth® MV Pre Dip	RT	1 min
Neoganth® MV Activator	40 °C	4 min
Neoganth® MV Reducer	30 °C	3 min

C. Electroless Copper Plating

The plating electrolytes Ecoganth® MV G2 and Printoganth® MV TP1 were prepared according to their technical datasheets. In both cases, a working temperature of 34 °C was applied. Air agitation was used permanently, regardless if plating was carried out or not. After a new make-up of the copper or after idle times, dummy plating was carried out: Therefore FR4 panels were cleaned, activated and immersed into the electroless copper solution (load = 0.5 to 2 dm^2/L cb) for a period of 30 minutes. Subsequently, the processing of test substrates was performed. The plating time was typically 30 min for Ecoganth® MV G2 and 20 min for Printoganth® MV TP1, if not stated otherwise. Before plating, analysis of the copper baths and chemistry replenishment was carried out according to the technical datasheets. After plating, the samples were washed with DI water and dried.

D. Evaluation of the Copper Deposits

Thickness Measurements: Thickness determinations by XRF were performed on a Helmut Fischer XDEV-SSD device. Measurements on FR4 material could be carried out directly. In the case of ABS test coupons, the copper film of one substrate side had to be removed by a strongly adhesive tape prior to measurement. Thickness measurements by FIB/SEM were done using a two-step procedure. First, the copper layer was opened by a focused ion beam. In the second step thickness determination was carried out by SEM. The analysis was performed on a FEI Nova NanoLab 600 DualBeam.

Backlight test: The backlight coupons contained holes arranged in 4 to 5 lines with 8 to 10 holes in a row. One line was separated from the remaining coupon using a pincer. The holes were opened to their half by grinding. On the other side of the sample, material was removed by grinding in such a way that a final distance of about 2 mm to the holes was achieved. The coupons were evaluated using an optical microscope (Olympus SZX12). Light was transmitted through the samples. Defects in the copper layers can be recognized as white spots.

Adhesion: For peel-strength measurements, electroless copper films were thickened by galvanic copper plating (30 µm galvanic copper) and subsequently baked for 1 hour at 150 °C. Stripes (broadness = 1 cm) were cut out from the panel. The adhesion of the copper to the substrate was measured by a peel-strength machine (Chatillon LTCM-6). The peel-off speed was 50.8 mm/min.

Adhesion tests by LUMiFrac® (LUM GmbH, Berlin) were performed using the adhesion analyzer LUMiFrac® 200. Metallic weights were glued on the surface of small PCB samples that were previously treated by an electoless copper electrolyte. The centrifugal force needed to cause delamination of the copper was determined.

Electrical reliability: Solder shock test: The electroless copper films on the solder shock test coupons were thickened by plating of 40 µm galvanic copper (Cupracid AC, 2 A/dm^2) on top. The substrates were washed with DI water and dried. Through-holes arranged in lines were covered by application of ~ 3 mm broad stripes of adhesive tape. The exposed surface copper was removed by etching using conc. HNO_3 : H_2O 1:1 (v/v). The substrates were again washed with DI water, dried and baked in an oven for 6 hours at 140 °C. Subsequently, thermal shocking using a tin/lead bath was carried out at a temperature of 288 °C. The substrates were floated on the tin surface six times for a period of 10 seconds and afterwards allowed to cool down to room temperature again. Each side was shocked three times in alternating order. The samples were embedded in a resin matrix, the holes were opened by grinding and the surface was polished. The interconnections were finally investigated using an optical microscope.

Daisy chain test: On top on the deposited electroless copper film a layer of 12 µm galvanic copper was plated. Structuring of the copper surface was carried out by using an industrial dry-film based etching process. Evaluation of the panel was done by investigation of the electrical conductivity of the daisy chains using a multimeter.

Throwing power: Lines of BMVs were isolated from the test coupon by milling or grinding. The substrates were embedded in a liquid resin matrix and cured. The BMVs were opened by grinding and investigated by SEM (Zeiss FE-SEM Ultra). Three measurements were carried out to determine a single layer thickness at a position. Three BMVs were investigated on each sample.

IV. Conclusion

In summary, we have shown that today's sophisticated technical requirements for an electroless copper electrolyte, can successfully be met using a new formaldehyde-free alternative. The presented process is robust and achieves comparable performance as formaldehyde-containing standards in terms of substrate coverage and adhesion, reliability, throwing power and lifetime. We are confident that the novel formulation provides a sustainable and secure alternative for mass production in the electronics industry.

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