
ELECTROLESS, NICKEL-FREE COPPER PLATING SOLUTION AND METHOD USING
THE SOLUTION

Field of the Invention

The present invention relates to an electroless copper plating solution for thin, preferably ultra-thin copper plating and a method for electroless copper plating utilizing said solution. The invention is suitable for manufacturing of fine line circuitry basing on SAP applications, in particular for the manufacture of printed circuit boards, IC substrates, high density interconnects and advanced package substrates.

Background of the Invention

The ongoing miniaturization of electronic devices requires sophisticated processes which allow for better line and space density (L/S) without adding significantly to the cost of the thus obtained devices. Line width and inter line distance of 10 μm (10 μm line and space – L/S) or less are currently difficult to achieve with high yield in high volume manufacturing, while sub-micron dimensions are commonplace when silicon processing methods are adopted.

A method for manufacture of fine line circuitry known in the art is the semi-additive process (SAP) which starts from a bare dielectric build-up layer as non-conductive substrate having on at least a portion of the back side a copper area which can be for example a contact area, and a second dielectric layer attached to the back side of the dielectric build-up layer. The substrate might comprise at least one opening such as a blind micro via can be formed by e.g. laser drilling in the build-up layer which extends through the substrate to the copper area on the back side of the build-up layer. The dielectric surface of the build-up layer can be subjected to a desmear process in the next step which leads to a roughened top surface of the build-up layer and a roughened surface of the dielectric side walls of the at least one opening. For subsequent metallization, an activation of the roughened top surface and the roughened side walls by e.g. depositing a noble metal containing activator is conducted. Next, a seed copper layer and/or a copper layer are deposited by electroless plating onto the activated top surface of the build-up layer and the activated side walls of the at least one opening. Such a resulting copper layer usually has a thickness of 0.8 μm to 1.5 μm which is required to provide a sufficient electrical conductivity on the activated surface for successive electroplating of copper. Further, a patterned resist layer e.g. a photoresist is provided onto the substrate and a thicker copper layer is then selectively electroplated into openings of resist wherein the copper is plated onto the electroless deposited copper surface of the build-up layer and walls. The patterned resist layer is then removed and those portions of the electroless deposited copper layer which are not covered by electroplated copper are

removed by differential etching. Such a process is for example disclosed in US 6,278,185 B1 and US 6,212,769 B1.

One disadvantage of the SAP method is the weak adhesion between the electroless deposited copper layer and the surface of the non-conductive substrate. The weak adhesion can lead to an undesired delamination of the copper tracks formed by subsequent electroplating of copper onto the electroless deposited copper layer in later manufacturing steps or later use of the printed circuit board.

Another disadvantage is the thickness of the electroless deposited copper layer, because during the removing/etching back the electroless deposited copper layer to separate the generated copper structures into lines and spaces, also the electroplated copper structures will be etched which causes undesired undercutting effects.

Following the requirements of a higher line and space density, the electroless copper plating procedure for SAP applications is becoming more and more demanding. Apart from the demand to provide of a nanovoid-free, bright and uniform copper layer, which is required for ultra-fine-line-and-space applications as explained above, the copper thickness plays a crucial role.

Thus, for providing the desired deposits, it is well known that additives must be added to an electroless copper bath to contribute to copper bath stability, copper deposit color, copper crystal structure and suppression of nanovoids. Without these additives the obtained copper layer growth is unpredictable and uncontrolled.

US 7,220,296 teaches an electroless plating bath comprising a water-soluble copper compound, glyoxylic acid and a complexing agent which may be EDTA.

US 2002/0064592 discloses an electroless bath comprising a source of copper ions, glyoxylic acid or formaldehyde as reducing agent, and EDTA, tartrate or alkanol amine as complexing agent.

However, the main challenge to deposit a uniform and thin electroless copper layer is the dwell time of the electroless copper plating step, which is typically in the range of 15-20 minutes, and which cannot be reduced below 10 minutes. Otherwise, a proper and efficient production flow for producing printed circuit boards cannot be ensured. On the other side, a long dwell time leads to thicker electroless copper layers.

Objective of the Invention

It is an objective of the present invention to provide an electroless, aqueous copper plating solution for thin copper plating and a method for electroless copper plating of a thin copper layer using the electroless, aqueous copper plating solution, which overcome the above-mentioned problems.

It is in particular an objective of the present invention to provide stable aqueous copper plating solution showing no passivation over a sufficient plating time. In addition, it is an objective of the present invention to provide a way to obtain very uniform, bright, nanovoid-free and salmon pink shining copper layers. It is furthermore an objective that said copper layer can also be utilized in SAP applications to produce fine line structures having L/S densities of less than 10/10 μm .

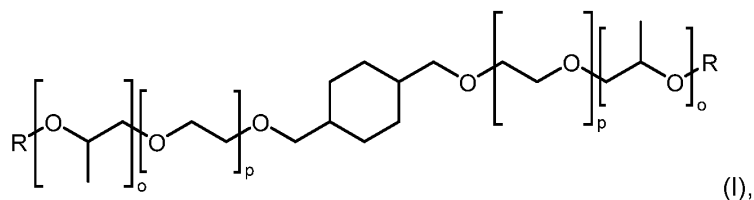
It is another object of the invention to provide a way to obtain a good adhesion between the substrate and the electroless plated copper layer.

It is an additional objective of the present invention to provide a plating solution and a method for thin copper plating such that the invention shows a self-limiting plating behavior which shows improved stability, stops depositing of the copper layer at a certain layer thickness, while the solution does not show self-passivation. The invention also shall avoid dummy plating.

Summary of the Invention

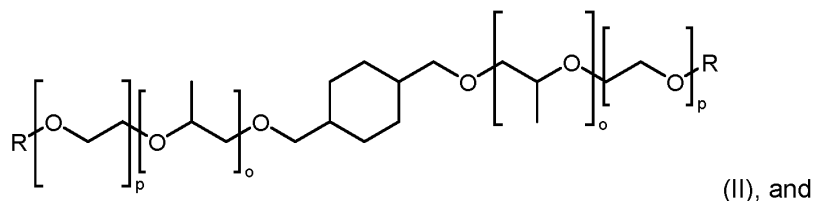
These objectives are solved by an electroless, aqueous copper plating solution for thin copper plating, comprising or consisting of:

- a source of copper ions;
- a reducing agent, selected from group consisting of formaldehyde, glyoxylic acid, and a source thereof;
- a source of tartrate ions as complexing agent;
- a modifier agent, selected from the group consisting of an EO-PO-block-copolymer comprising EO- and PO-units according to formula I

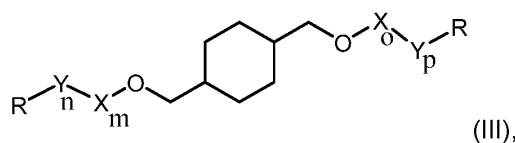


a PO-EO-block-copolymer comprising EO- and PO-units according to formula II

(II),



an EO-/PO-random-copolymer according to formula III



wherein X and Y are randomly and independently selected EO- or PO-units, wherein at least one EO- and PO-unit is present in formula (III), and mixtures of said polymers thereof, wherein

- R is hydrogen, allyl or C₁-C₄-alkyl, preferably hydrogen, methyl, butyl, allyl, more preferably R is hydrogen, methyl and butyl, most preferred hydrogen or methyl,
- m, n, o, and p are independently selected integer from 1 – 20, preferably from 5 – 18, more preferably from 10 – 16;
- having a pH value from 12 – 14; and
- the solution does not contain nickel ions and any other complexing agent.

In the context of the present invention an EO-unit is an ethylene oxide monomer unit, and a PO-unit is a propylene oxide monomer unit as shown e.g. in formula (I).

Furthermore, the additional objective is solved by a method for electroless copper plating of a thin copper layer, the method comprises the following steps in the following order:

- (i) providing a non-conductive substrate comprising an activated surface;
- (ii) contacting the substrate with an electroless aqueous copper plating solution according to the present invention;
- (iiia) self-limiting plating of a thin copper layer of a thickness of 60 – 150 nm onto the activated surface, wherein if the thickness of 60 – 150 nm is reached the plating speed of the solution is automatically reduced preferably to less than 0.009 nm/s, preferably less than 0.005 nm/s, or
- (iiib) self-limiting plating of a thin copper layer onto the activated surface, wherein after 20 min, the plating speed of the solution is automatically reduced preferably to less than 0.009 nm/s, preferably less than 0.005 nm/s.

One or more of the above-mentioned objects are achieved by the electroless copper plating solution and the method using the electroless copper plating solution (hereinafter abbreviated as the "solution") according to the invention, or by advantageous embodiments as described in dependent claims and the description.

The invention provides an electroless copper plating solution capable of depositing thin electroless copper in a controlled manner, while showing also required properties, like nanovoid-free deposition, salmon-pink copper color and reliability, which are additionally required for a well-performing electroless copper plating solution. The inventive solution enables plating until a smooth, thin and uniform electroless copper layer is achieved, regardless of the substrate and its roughness and without any need for dummy plating.

The invention also shows a self-limiting behavior during the plating process even if copper ions and tartrate ions are replenished. That means, once a uniform electroless copper layer is deposited the copper deposition rate reduces to a minimum, yet the solution does not drift into passivation. In particular, after a thickness of the electroless plated copper layer of 60-150 nm, preferably 60-120 nm, is reached, no significant further copper plating can be achieved onto the electroless plated substrate. This facilitates on the one hand the handling of the substrate within the overall full-automated production process, because the treated substrates need to wait sometimes to be processed in the next step while the thickness will not increase further. On the other, the thickness which is achieved within 20 min perfectly fits to the intended use in SAP applications and there is no need for strict plating time control.

The solution and the method of the invention can be used for deposition of copper on surfaces, in trenches, blind-micro-vias, through-hole-vias, and comparable structures of the non-conductive surface in the manufacturing of printed circuit boards, chips, carriers, wafers and various other interconnect devices.

The term "thin" in the context of the present invention means that the deposited electroless copper layer is in particular suitable for a subsequent SAP application to build line to space dimension of less than 10/10 μm . Thus "thin copper layer" is understood as having a thickness from 60 – 200 nm.

The solution of the invention is an aqueous solution. The term "aqueous solution" means that the prevailing liquid medium, which is the solvent in the solution, is water. Further liquids, that

are miscible with water, as for example alcohols and other polar organic liquids, may be added.

The solution of the present invention may be prepared by dissolving all components in aqueous liquid medium, preferably in water.

“Complexing agent” in the context of the present invention means that the complexing agent and the concentration of the complexing agent is intentionally added to the solution to complex the copper ions in the electroless copper plating solution.

C₁-C₄-alkyl for includes methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl.

The terms “layer” and “deposits” can be used interchangeably.

The solution contains a copper ion source, which may for example be any water soluble copper salt. Preferably the source of copper ions is selected from the group consisting of copper chloride, preferably copper(II) chloride, more preferably copper(II) chloride dihydrate, and copper(II) tartrate, more preferably the source of copper ions is copper(II) chloride-and/or copper(II) chloride tartrate. Most preferably copper(II) chloride dihydrate is used. If copper(II) tartrate is used, the respective tartrate ions concentration will be part of the overall tartrate concentration of the solution.

In one embodiment of the invention, the concentration of the copper ions is from 0.04 - 0.08 mol/L, preferably 0.05 - 0.07 mol/L.

The solution of the invention contains as a complexing agent, a source of tartrate ions, preferably any water-soluble tartrate ions are suitable. Preferably the source of tartrate ions is selected from the group consisting of sodium tartrate and potassium tartrate. More preferably Rochelle salt (potassium sodium tartrate) is used. Preferably, tartrate ions are the only complexing agent in solution of the invention. More preferably, the solution is free of any other complexing agent.

In one embodiment of the invention, the concentration of the tartrate ions is from 0.10 – 0.24 mol/L, preferably from 0.14 – 0.19 mol/L.

The reducing agent serves for reducing the copper ions in order to obtain metallic copper for plating. The reducing agent is selected from the group consisting of formaldehyde, glyoxylic acid, and a source thereof. Preferably, the reducing agent is formaldehyde.

In one embodiment of the invention, the concentration of the reducing agent is from 0.10 - 0.22 mol/L, preferably 0.12 - 0.20 mol/L.

The term "source of a reducing agent" means a substance that is converted to a reducing agent in the solution. The source is for example a precursor of a reducing agent that is converted to the reducing agent. An example is given below with respect to glyoxylic acid.

The term "source of glyoxylic acid" encompasses all compounds that can be converted to glyoxylic acid in aqueous solution, such as precursors. A preferred precursor is dichloroacetic acid. Glyoxylic acid is the reducing agent for the reduction of copper ions to elementary copper. In the solution, glyoxylic acid and glyoxylate-ions may be present. As used herein the term "glyoxylic acid" includes salts thereof. The exact nature of the species, acid or salt, present will depend on the pH of the solution. The same consideration applies to other weak acids and bases.

Electroless copper plating solution using reducing agents described above employs a pH, between 12 and 14, preferably between 12.3 and 13, and are adjusted generally by potassium hydroxide (KOH) or sodium hydroxide (NaOH). Thus, the solution may contain a source of hydroxide ions, as for example and without limitation one or more of the compounds listed above. A source of hydroxide is for example added if an alkaline pH of the solution is desired and if the pH is not already in the alkaline range by other constituents.

The solution of the present invention further comprises a modifier agent according to formula (I), (II) and (III).

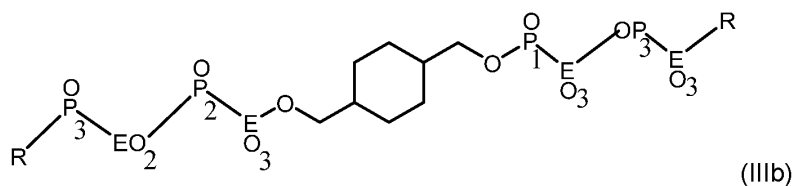
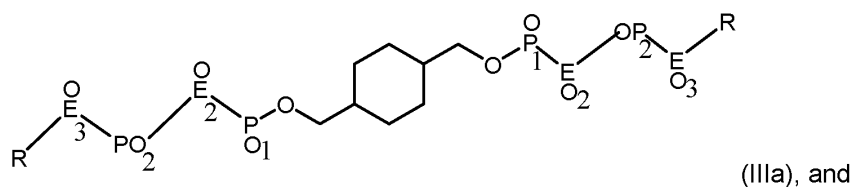
In one embodiment of the invention, the molecular weight of the modifier agent is from 400 – 5,600 Da, preferably from 800 – 1,900 Da, more preferably from 1,200 – 1,800 Da.

Preferred is a modifier agent according to formula (I) wherein each o is 8 and each p is 8. More preferred is a modifier agent according to formula (I) wherein the molecular weight is 1.800 Da.

Preferred is a modifier agent according to formula (II) wherein each o is 3 and each p is 8.
More preferred is a modifier agent according to formula (II) wherein the molecular weight is 1.300 Da.

A modifier agent according to formula (III) has randomly attached (ethoxylated, propoxylated) EO- and PO-units wherein a sequence of these units can e.g. contain EO-units as mono-, di- or tri-units followed independently by PO-units of mono-, di- or tri-unit. X_n and Y_m can have the same sequence as X_o and Y_p or all X_n , Y_m , X_o , Y_p can be different.

As examples of a modifier agent according to formula (III) the following modifier agents according to formula (IIIa) and (IIIb) are shown.



Preferred is a modifier agent according to formula (III) wherein each o is 8 and each p is 8.
More preferred is a modifier agent according to formula (III) wherein the molecular weight is 1.800 Da.

In one embodiment of the invention, the concentration of the modifier agent is from 0.01 – 0.10 mmol/L, preferably 0.03 – 0.08 mmol/L.

Preferably, the solution of the present invention does not contain nickel ions or any other metals or metal ions which can be reduced with the reducing agent. It was found that nickel has to be avoided, because it shows negatively effects of the desired copper deposition. Moreover, the presence of nickel in the bath would lead to the elimination of the self-limiting properties of the solution. More preferably, the solution does not contain any further metals or metal ions if not explicitly named in the description as sodium ions or potassium ions.

Preferably, the solution of the present invention does not contain sulfate ions. It was found that sulfate has a negative effect on bath stability and quality of the deposited electroless copper layer.

Preferably, the solution of the present invention does not contain any further organic components, as for example stabilizers, surfactants, additives, as rate controlling additives, grain refining additives, pH buffers, pH adjusters, and enhancers.

In another aspect, the present invention relates to a method for electroless copper plating of a thin copper layer, the method comprising the steps (i) to (iiia,b) as described above. The method provides a deposited thin copper layer which is conformal and void-free plated onto the activated surface.

In a preferred method of the invention, the (iiia) self-limiting plating is conducted for up to 20 min, preferably 5 – 18 min, more preferably 5 – 15 min wherein the thickness of 60 – 120 nm is reached.

In a preferred method of the invention, the (iiib) self-limiting plating is conducted the plating speed of the solution is automatically reduced to less than 0.005 nm/s, preferably less than 0.003 nm/s preferably after 5 – 18 min, more preferably after 5 – 15 min wherein the thickness of 60 – 120 nm is reached in that time.

With other words, the plating speed to reach the mentioned copper thickness of the electroplated copper layer is reduced by > 80 % compared to the subsequent plating speed after reaching said thickness of 60 – 120 nm.

In a preferred method of the invention, the (iiia) self-limiting plating or (iiib) self-limiting plating is conducted at a temperature of 27°C – 34°C.

The plating speed reduction after reaching the thickness of 60 – 120 nm in step (iii) is not affected by the concentration of the copper ions and tartrate ions and cannot be accelerate by adding copper ions and/or tartrate ions.

The method can be conducted in a plating equipment wherein substrate is conveyed vertical or horizontal and treated by e.g. spraying with, flooding with, or immersion in the solution of the invention.

One envisaged application of the method is the preparation of printed circuit boards. The electroless deposition of copper according to the method of the invention can particularly be used for the through-plating of holes, surfaces, trenches, blind micro vias in printed circuit boards. Double sided or multilayer boards (rigid or flexible) may be plated by means of the present invention.

The method of the invention produces copper layers on the substrate with a roughness, expressed as the root-mean-square roughness parameter, of 5 nm to 60 nm, preferably 5 nm – 55 nm and more preferably 10 nm – 45 nm. The roughness of the copper layer is determined with white light interferometry, as described in the examples.

Non-conductive substrates that are generally used with the invention are substrates, in particular a dielectric substrate having at least one dielectric surface to be treated, comprises organic polymers selected from resins and/or plastics, and blends thereof, wherein resins and plastics are more preferably selected from the group consisting of epoxy resin, isocyanate resin, bismaleimide triazine resin, phenylene resin, polyester, even more preferably selected from polyethylene terephthalate (PET), polyimide (PI), polytetrafluorethylene, acrylonitrile-butadiene-styrene (ABS) copolymer, polyamide (PA), polycarbonate (PC), liquid crystal polymer (LCP) as cyclic olefin copolymer (COC), Ajinomoto build-up films (ABF, ABF/epoxy-type substrate), flame resistant PCB material (as FR3, FR4) or plastics made for photo-imageable dielectrics as well as mixtures and blends of the aforementioned, or a composite basing on a mixture of glass fillers and/or silica fillers and/or glass fabrics with said organic polymers. The substrate can also be a glass substrate or a silicon substrate.

In a preferred embodiment of the method of the present invention, the method further comprises after step (iia,b) the following steps in the following order to obtain fine-line-and-space structures of $< 8/8 \mu\text{m}$, preferably $< 4/4 \mu\text{m}$:

- (iv) depositing a photoresist layer onto the thin copper layer;
- (v) structuring the photoresist layer and creating fine-line-and-space opening within the photoresist which are ending onto the copper layer;
- (vi) electrolytic or electroless filling the fine-line-and-space opening with copper;
- (vii) removing the remaining photoresist; and
- (viii) etching back the copper layer of step (iii) in order to obtain the fine-line-and-space copper structures.

The inventive method is preferably used for a semi-additive process (SAP) for the manufacturing of ultra-fine-line-and-space copper structures of $< 8/8 \mu\text{m}$, preferably $4/4 \mu\text{m}$.

In one embodiment, a pretreatment process sequence before step (i) of the inventive method can be conducted. The non-conducted substrate can comprise through holes or blind holes (also named as blind micro vias).

An exemplary and non-limiting pretreatment process for pretreatment the non-conductive substrate, e.g. for printing circuit board laminates and other suitable substrates, which is known to a skilled person, may comprise one or more of the following steps

- a) optionally cleaning and conditioning the substrate to increase adsorption. With a cleaner, organics and other residues are removed. It may also contain additional substances (conditioners) that prepare the surface for the following activation steps, i.e. enhance the adsorption of the catalyst and lead to a more uniformly activated surface,
 - b) etching, to remove oxides from the surface of the copper, especially from inner layers in holes which are accessible after drilling blind vias which ends at these inner copper layers. This may be done by persulphate or peroxide based etching systems,
 - c) contacting with a pre-dip solution, such as a hydrochloric acid solution or sulfuric acid solution, optionally with an alkali metal salt, such as sodium chloride, also in the pre-dip solution.
 - d) contacting with an activator solution, that contains colloidal or ionic catalyzing metal, such as a noble metal, preferably palladium, causing the surface to become catalytic. The pre-dip in step c) serves to protect the activator from drag-in and contaminations, and optionally, particularly if the activator contains ionic catalyzing metal,
 - e) contacting with a reducer, wherein the metal ions of an ionic activator are reduced to elemental metal.
- or, if the activator contains colloidal catalyzing metal,
- f) contacting with an accelerator, wherein components of the colloid, for example a protective colloid, is removed from the catalysing metal.

Steps d), e) and f) are conducted to provide the non-conductive substrate comprising an activated surface according to step (i) of the method of the present invention.

In alternative kind of process steps a permanganate etching step can be employed. The so-called desmear process is a multi-stage process, the steps of which are a swelling step, a permanganate etching step and a reduction step. The sweller used in the swelling step is

made of a mixture of organic solvents. During this step drill smear and other impurities are removed from the surfaces of the substrate. A high temperature of 60 - 80 °C promotes the infiltration of the sweller which leads to a swelled surface. Therefore a stronger attack of the subsequently applied permanganate solution is possible during the permanganate etching step. Afterwards the reduction solution of the reduction step removes the manganese dioxides produced during the permanganate step from the surfaces. The reduction solution contains a reducing agent and optionally a conditioner.

The desmear process may also be combined with the above-described steps a) to f). The desmear process may be performed before step a) of the above-described pretreatment process or the desmear process may be performed instead of steps a) and b) of the above-described pretreatment process.

Still another process, which is often used for glass substrates, may be carried out with following steps before copper plating: A glass surface that is to be plated exhibits metal seed layers. The metal seed layers may be brought onto the surface by sputtering techniques. Exemplary seeds are layers composed of copper, molybdenum, titanium, or a mixture thereof. Said pretreated glass surface is contacted with an activator solution that contains ionic catalyzing metal, such as a noble metal, preferably palladium, causing the surface to become catalytic. The ionic catalyzing metal is reduced onto the surface by the seed metal. In this process, addition of a further reducer may be omitted. This process is especially used in copper plating of glass substrates for display applications.

The exemplary pretreatment processes, or single steps thereof, may be combined to alternative pretreatment processes, if found necessary.

DESCRIPTION OF FIGURES

- Fig. 1 Cross-sections of the plated electroless copper layers on ABS and ABF coupons
- Fig. 2 SEM image of wedge of a blind micro via of an ABF/GX-T31 coupon
- Fig. 3 Top-view of SEM image of a copper layer on ABF/GX-T31 coupon after 15 min and eight hours

Examples

The invention is now described in further detail by the following examples. These examples are set forth to illustrate the present invention but should not be construed as limiting the present invention.

Preparation of the test coupons made of ABS and ABF

ABS, ABF (drilled GX-T31) and ABF (undrilled GX-92 R) test coupons (Table 1) were used for the assessment of the quality of the electroless copper layer. The parameters tested were appearance, copper morphology, deposit thickness, roughness of the deposited copper layer, throwing power and peel strength.

Table 1. Base materials used for the assessment of the electroless copper layer quality and parameters tested.

Material name	Material Type	Test parameter
Metak	ABS	Appearance; copper morphology; copper thickness; roughness
ABF	ABF/GX-92 R	Appearance; copper morphology; copper thickness; roughness; peel strength
ABF	ABF/GX-T31 ^a	Throwing power

^aBlind microvia diameter = 60 μm

ABF Lamination and Preparation Conditions

ABF/GX-92 R prepregs were laminated onto Bondfilm[®]-treated copper-clad FR4 panels using a Dynachem VA 7124-HP6 vacuum laminator (lamination conditions: 30 s vacuum time, 30 s dynamic slap-down time, 20 s static slap-down time, 2.0 mbar vacuum set point, 5.0 kg/cm² pressure). Immediately after this the laminated panels were semi-cured in an air-circulated oven.

Pretreatment: Desmear Conditions

The coupons requiring the desmear process were desmeared (desmear process) using the Securiganth[®] series of treatment baths listed in Table 2 (available by Atotech Deutschland GmbH & Co. KG), which were operated on a small pilot line scale (15-22 L) at typical bath settings.

Table 2. ABF/GX-T31 and ABF/GX-92 R desmear conditions.

Step ^a	Bath	Immersion time [s]
1	Securiganth [®] MV Sweller	120
2	Securiganth [®] MV P-Etch	240 ^b /480 ^c /600 ^d
3	Securiganth [®] MV Reduction Conditioner	120

^aDI water cascade rinses of approximately 60 s between each step for rinsing. ^bABS coupons. ^cABF/GX-T31 coupons. ^dABF/GX-92 R coupons.

Activation and Electroless Copper Conditions

Prior to electroless copper plating, all test coupons were treated with the Securiganth® and Neoganth® series of baths shown in Table 3 (available by Atotech Deutschland GmbH & Co. KG), which were operated on a beaker-scale (2 L) at typical bath settings.

Table 3. Pretreatment and activation conditions applied to ABF/GX-T31 and ABF/GX-92 R coupons.

Step ^a	Bath	Immersion time [s]
1	Securiganth® MV Cleaner PF	240
2	Neoganth® MV Etch Cleaner SPS	60
3	Neoganth® MV Pre Dip	60
4	Neoganth® MV Activator	240
5	Neoganth® MV Reducer	180

^aTap water rinse of approximately 60 s between each step, except between steps 3 and 4.

The electroless copper plating was done with the electroless copper plating solution of **Inventive Example 1** which was made up fresh and used immediately after heating up to 28 °C.

The used electroless copper plating solution comprised the following concentrations:

Inventive Example 1

Tartrate ions: 0.14 mol/L Rochelle salt

Copper ions: 0.05 mol/L (copper(II) chloride dihydrate)

pH: 12.3 adjusted with sodium hydroxide

Formaldehyde: 0.12 mol/L

Modifier agent according to formula (III) with a molecular weight of 1800 Da: 0.03 mmol/L

Before the test coupons were immersed in the bath, dummy plating was done for 10 minutes with two 10 cm × 10 cm FR4 bare laminate coupons. Although dummy plating is not necessary for the electroless copper plating solution, it was done so as to emulate typical customer process conditions, under which dummy plating is usually carried out. All test coupons for the deposit thickness investigations were immersed into the electroless copper plating solution at once and the coupon sampling intervals were 15 minutes and 1, 2, 4, 6

and 8 hours. The removed coupons were not replaced by fresh coupons, meaning the bath loading progressively decreased. The solution was analyzed every hour and the consumed bath components replenished accordingly. Peel strength and throwing power coupons were plated in a separate bath for 15 minutes.

Copper Morphology Investigation, copper Thickness Determination, Roughness Measurement and Throwing Power Assessment

For the investigations of the copper morphology and copper thickness focused ion beam (FIB) and field emission scanning electron microscopy (FESEM) were utilized (FEI Helios NanoLab 660i; resolution: 10,000x, 25,000x and 50,000x for copper surface investigations, respectively 50,000x for copper thickness). A scanning electron beam at 3 kV acceleration voltage and a current of 0.20 nA were applied. The surface roughness was determined by using interference microscopy. For the throwing power assessment, appropriately microsectioned ABF/GX-T31 coupons were investigated by FESEM. The Olympus Stream software (Version 2.2) was used for all image processing.

Peel Strength Coupon Preparation and Test Conditions

After electroless copper plating, the ABF/GX-92 R coupons were annealed at 140 °C for 30 minutes and, after cooling to room temperature, reinforced with 35 µm of copper using a standard electrolytic copper bath. After rinsing and drying the coupons with compressed air they were fully cured at 190 °C for 60 minutes and afterwards routed into strips of 1 cm width. The force required to peel the copper film from these coupons was measured using an Erichsen Unimat Plus 050-2kN material testing machine equipped with a 20 N load cell, at a peeling speed of 50.8 mm/min while always ensuring a peeling angle of 90°.

Results of the Inventive Example 1

After plating with the inventive electroless copper plating solution onto ABS and ABF/GX-92 R coupons as non-conductive substrate as described above, the copper layer thickness was determined, and the results are summarized in Table 4. It can be seen that the copper plating solution could plate continuously for 8 hours without running into passivation. Further the copper plating solution shows a self-limiting effect and a strongly decelerated copper deposition speed. The copper plating solution already reaches its target thickness after 15 minutes and then it slows down significantly but does not stop plating entirely. The electroless copper thickness achieved with the electroless copper solution after eight hours is twice as thick as that obtained after 15 minutes for ABF/GX-92 R and slightly more than twice as thick for ABS.

Table 4. Absolute copper deposit thicknesses of the solution on ABS and ABF.

Plating time [h]	Cu layer thickness [μm]	
	on ABS	on ABF
0.25	0.08	0.11
1	0.10	0.12
2	0.13	0.14
4	0.14	0.15
6	0.17	-
8	0.18	0.22

Table 4 also shows that the copper layer thicknesses on ABF/GX-92 R are somewhat thicker compared to those which were obtained on ABS. This gives the first indication of the solution's leveling effect. Since the roughness of these two base materials is slightly different after the desmear process (ABS: $S_a = 50\text{-}60\text{ nm}$; ABF/GX-92 R: $S_a = 70\text{-}80\text{ nm}$) it seems that the electroless copper plating solution plates at a certain rate until a uniform electroless copper layer is reached and all crevices have been filled. Thus, the final copper thickness is slightly higher for the rougher ABF/GX-92 R material and only after said crevices have been filled does the deposition speed slow down.

The roughness investigations of the electroless copper surfaces evince that the roughness of the plated electroless copper does not change significantly with plating time (Table 5). This indicates as well that the single components of the solution interact with each other in a way that facilitates the electroless copper deposition to not take place randomly but rather in a controlled manner on predilected areas on the surface. The copper roughness results furthermore suggest that the smoother the base material the smoother the electroless copper surface. These results reinforce the hypothesis that the solution shows a pronounced leveling effect.

Table 5: Roughness investigations of the electroless copper surfaces

Plating time [h]	Surface Roughness [nm]	
	on ABS	on ABF
0.25	61.46	81.32
1	57.67	67.68
2	65.39	75.17
4	64.80	87.29

6	77.93	101.25
8	66.85	105.46

Fig. 1 shows cross-sections of the plated electroless copper layers on ABS and ABF/GX-92 R coupons. The electroless copper solution demonstrates smooth electroless copper growth on both materials and even the smallest crevices of the rougher ABF material, where exposed glass fillers contribute additionally to the surface structure, are filled.

The ability to plate reliably in such small crevices indicates that an excellent throwing power can also be expected from this electroless copper solution and this is shown in Figure 2. It is clearly visible that the electroless copper solution can reach the entire wedge, despite its narrowness, and can reliably plate its target thickness.

Figure 3 depicts the surfaces of the deposits obtained after 15 minutes and after eight hours of plating in the electroless copper solution on ABS at a larger magnification of 50000× to investigate the crystal structure in more detail. It can be stated that regardless of plating time, well-defined copper crystals, even cubic ones, of nanoscopic size are readily discernible, which suggests that from the very beginning the deposit is of high purity and that the incorporation of the additive is minimal if at all present. It is also expected that such a surface structure will be beneficial for dry-film adhesion.

The well-defined copper crystal structure seems to be also favorable for satisfying peel strength results. The obtained peel strength for the above-mentioned test conditions is 4.55 N/cm $\pm$ 1.15. With respect to the low roughness of Sa = 70-80 nm for the ABF/GX-92 R material, this value can be considered as good. Since the demand of having smooth surfaces is growing it is indispensable to have an electroless copper solution which is reliable depositing in all crevices to ensure a good copper to copper and a good copper to base material connection and is acting like an anchor.

As mentioned above, the final thickness is reached already after 15 minutes. Thereafter the deposition speed slows down to a minimum and continues to stay slow. This allows the assumption that two different deposition mechanisms are at work, which seem to change with the modification of the surface. At the very beginning of the deposition process, the surface of the freshly activated test coupon is covered with a palladium seed layer and the complexed Cu²⁺ ions are reduced and deposited in a relatively unhindered fashion on the palladium seed layer. Once a continuous copper layer is formed, we assume that the solution components interact with each other and with the copper surface in a manner that facilitates leveling of the deposited layer. We further assume that in areas in which the concentration of

the species formed by this solution component/surface interaction is high, the subsequent reduction of Cu^{2+} to Cu^0 cannot take place easily, thus resulting in the leveling effect.

Investigations to elucidate the assumptions mentioned above are ongoing, but it can nevertheless be concluded that this newly invented electroless copper solution features leveling properties in combination with an additional self-limiting plating effect. We propose that this can be considered as a smart plating behavior.

Comparative Example 1

ABS coupon were treated in the same way as above explained for the Inventive Example 1. The comparative electroless copper plating was done with the electroless copper plating solution of **Comparative Example 1** wherein the tartrate ions were substituted by EDTA as complexing agent. The solution according to Inventive Example 2 was used to compare. The comparative solution and the inventive solution were made up fresh and used immediately after heating up to 28 °C.

The used solutions comprised the following concentrations and:

Comparative Example 1

EDTA: 0.05 mol/L

Copper ions: 0.05 mol/L (copper(II) chloride dihydrate)

pH: 12.3 adjusted with sodium hydroxide

Formaldehyde: 0.12 mol/L

Modifier agent according to formula (III) with a molecular weight of 1776 Da: 0.03 mmol/L

Inventive Example 2

Tartrate ions: 0.14 mol/L Rochelle salt

Copper ions: 0.05 mol/L (copper(II) chloride dihydrate)

pH: 12.3 adjusted with sodium hydroxide

Formaldehyde: 0.12 mol/L

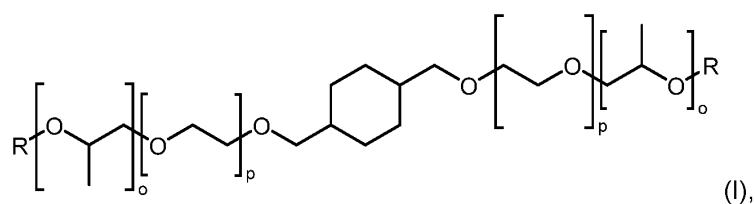
Modifier agent according to formula (III) with a molecular weight of 1776 Da: 0.03 mmol/L

The deposit obtained within 15 minutes on ABS coupons from the Comparative Example 1 bath composition was 170 nm thick and had a dark, brownish appearance. Thus, this bath is unsuitable for the field of application for which the object of the present invention is intended. The deposit obtained within 15 minutes on ABS coupons from the Inventive Example 2 bath

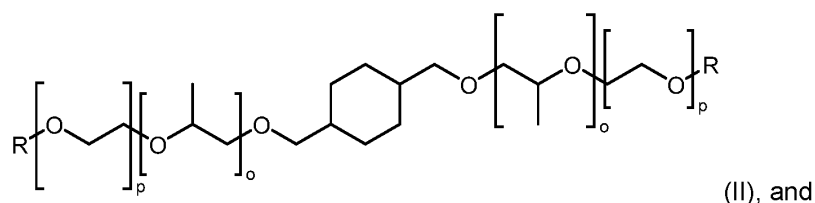
composition on the other hand was 80 nm thick and had a bright, salmon-pink appearance, thus performing as required.

Claims

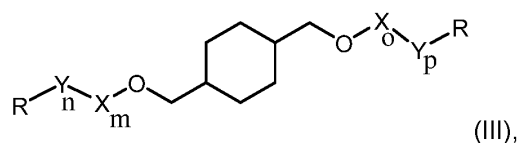
1. An electroless, aqueous copper plating solution for thin copper plating, comprising or consisting of:
- a source of copper ions;
 - a reducing agent selected from the group consisting of formaldehyde, glyoxylic acid, and a source thereof;
 - a source of tartrate ions as complexing agent;
 - a modifier agent, selected from the group consisting of an EO-PO-block-copolymer comprising EO- and PO-units according to formula I



a PO-EO-block-copolymer comprising EO- and PO-units according to formula II (II),



an EO-/PO-random-copolymer according to formula III



wherein X and Y are randomly and independently selected EO- or PO-units, wherein at least one EO- and PO-unit is present in formula (III), and mixtures of said polymers thereof, wherein

- R is hydrogen, allyl or C₁-C₄-alkyl,
- m, n, o, and p are independently selected integer from 1 – 20;
- having a pH value from 12 – 14; and
- the solution does not contain nickel ions and any other complexing agent.

2. The electroless, aqueous copper plating solution according to claim 1, wherein the solution does not contain any other organic compounds and/or metal ions.
3. The electroless, aqueous copper plating solution according to claim 1 or 2, wherein the concentration of the tartrate ions is from 0.10 – 0.24 mol/L, preferably from 0.14 – 0.19 mol/L and/or the concentration of the copper ions is from 0.04 - 0.08 mol/L, preferably 0.05 - 0.07 mol/L.
4. The electroless, aqueous copper plating solution according to one of the preceding claims wherein the reducing agent is formaldehyde.
5. The electroless, aqueous copper plating solution according to one of the preceding claims wherein the source of copper ions is copper(II) chloride- and/or copper(II) tartrate.
6. The electroless, aqueous copper plating solution according to one of the preceding claims wherein the concentration of the modifier agent is from 0.01 – 0.10 mmol/L, preferably 0.03 – 0.08 mmol/L.
7. The electroless, aqueous copper plating solution according to one of the preceding claims wherein the molecular weight of the modifier agent is from 400 – 5,600 Da, preferably from 800 – 1,900 Da, more preferably from 1,200 – 1,800 Da.
8. A method for electroless copper plating of a thin copper layer, the method comprises the following steps in the following order:
 - (i) providing a non-conductive substrate comprising an activated surface;
 - (ii) contacting the substrate with an electroless aqueous copper plating solution according to one of claims 1 - 3;
 - (iia) self-limiting plating of a thin copper layer of a thickness of 60 – 150 nm onto the activated surface, wherein if the thickness of 60 – 150 nm is reached the plating speed of the solution is automatically reduced preferably to less than 0.009 nm/s, preferably less than 0.005 nm/s, or
 - (iib) self-limiting plating of a thin copper layer onto the activated surface, wherein after 20 min, the plating speed of the solution is automatically reduced preferably to less than 0.009 nm/s, preferably less than 0.005 nm/s.

9. The method according to claim 8, wherein the non-conductive substrate is a substrate made from glass, ceramic, plastics or mixture thereof.
10. The method according to claims 8 or 9, wherein the step (iiia) self-limiting plating self-limiting plating is conducted for up to 20 min, preferably 5 – 18 min, more preferably 5 – 15 min wherein the thickness of 60 – 150 nm is reached.
11. The method according to claims 8 - 10, wherein step (iiia) self-limiting plating or the step (iiib) self-limiting plating is conducted at a temperature of 27°C – 34°C.
12. The method according to claims 8 - 11, wherein the plating speed reduction after reaching the thickness of 60 – 150 nm in step (iii) is not affected by the concentration of the copper ions and tartrate ions and cannot be accelerated by adding copper ions and/or tartrate ions.
13. The method according to claims 8 - 12, wherein the thin copper layer is conformal and void-free plated onto the activated surface.
14. The method according to claims 8 - 13, wherein the method further comprises after step (iii) the following steps in the following order to obtain fine-line-and-space structures of < 8/8 µm, preferably < 4/4 µm:
 - (iv) depositing a photoresist layer onto the thin copper layer;
 - (v) structuring the photoresist layer and creating fine-line-and-space opening within the photoresist which are ending onto the copper layer;
 - (vi) electrolytic or electroless filling the fine-line-and-space opening with copper;
 - (vii) removing the remaining photoresist; and
 - (viii) etching back the copper layer of step (iii) in order to obtain the fine-line-and-space copper structures.
15. The method according to claim 8 - 13, wherein the method is used for a semi-additive process (SAP) for the manufacturing of ultra-fine-line-and-space copper structures of < 8/8 µm, preferably 4/4 µm.