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(54) ELECTROLESS COPPER PLATING SOLUTION

STROMLOSE VERKUPFERUNGSLÖSUNG

SOLUTION DE DÉPÔT DE CUIVRE CHIMIQUE

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Description

[0001] The present invention relates to an electroless copper plating solution, a method for electroless copper plating utilizing said solution and the use of the solution for the plating of substrates.

[0002] Electroless plating is the controlled autocatalytic deposition of a continuous film of metal without the assistance of an external supply of electrons. Non-metallic surfaces may be pretreated to make them receptive or catalytic for deposition. All or selected portions of a surface may suitably be pretreated. The main components of electroless copper baths are the copper salt, a complexing agent, a reducing agent, and, as optional ingredients, an alkaline agent, and additives, as for example stabilizers. Complexing agents are used to chelate the copper to be deposited and prevent the copper from being precipitated from solution (i.e. as the hydroxide and the like). Chelating copper renders the copper available to the reducing agent which converts the copper ions to metallic form.

[0003] US 4,617,205 discloses a composition for electroless deposition of copper, comprising copper ions, glyoxylate as reducing agent, and a complexing agent, for example EDTA, which is capable of forming a complex with copper that is stronger than a copper oxalate complex.

[0004] 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.

[0005] 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.

[0006] GB 1 305 468 A discloses an electroless copper bath comprising at least two complexing agents, one of which is cyclohexane diaminetetraacetic acid. The other complexing agent can be any of a list of several complexing agents including Quadrol, HEDTA or EDTA.

[0007] Performance of a copper plating solution is difficult to predict and strongly depends on its constituents, especially the complexing agent and the reducing agent, and the molar ratio of its constituents.

[0008] An object of the invention was to provide with an electroless copper plating solution with improved performance, particularly an improved copper deposition rate. A further object of the present invention was to provide an electroless copper plating solution for obtaining copper deposits with low roughness.

[0009] The present invention provides with an electroless copper plating solution, comprising

- a source of copper ions,
- a reducing agent or a source of a reducing agent, and
- a combination comprising

    i) N,N,N',N'-Tetrakis (2-hydroxypropyl)ethylenediamine or a salt thereof, and
    ii) N'-(2-Hydroxyethyl)-ethylenediamine-N,N,N'-triacetic acid or a salt thereof, as complexing agents; and

wherein the ratio of the total molar amount of all complexing agents to copper ions is in the range of 1:1 to 10:1.

[0010] The combination of complexing agents may further comprise

iii) ethylenediamine tetraacetic acid or a salt thereof.

[0011] N,N,N',N'-Tetrakis (2-hydroxypropyl) ethylenediamine is hereinafter abbreviated as "Quadrol", which is a trademark of BASF company.

[0012] Ethylenediamine tetraacetic acid is hereinafter also named as "EDTA".

[0013] N'-(2-Hydroxyethyl)-ethylenediamine-N,N,N'-triacetic acid is hereinafter also named as "HEDTA".

[0014] In one embodiment the electroless copper plating solution preferably does not contain cyclohexane diamine tetraacetic acid (CDTA) in an amount ranging from 0.1 mM to 5.5 M. In another embodiment the electroless copper plating solution preferably does not contain CDTA at all.

[0015] One or more of the above mentioned objects are achieved by the electroless copper plating solution (hereinafter abbreviated as the "solution") according to claim 1, or by advantageous embodiments as described in dependent claims and the description. The copper plating solution of the invention shows an improved copper deposition rate. At the same time, a low roughness of copper surfaces can be reached, which is crucial for performance of certain electronic devices. Due to a higher deposition rate, a higher thickness of copper layer can be reached at the same process time.

[0016] The solution according to the invention and the method according to the invention are preferably used for the coating of printed circuit boards, chip carriers and semiconductor wafers or also of any other circuit carriers and interconnect devices. The solution is used in particular in printed circuit boards and chip carriers, but also in semiconductor wafers, to plate surfaces, trenches, blind micro vias, through hole vias (through holes) and similar structures with copper.

[0017] Particularly, the solution of the invention or 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 in printed circuit boards, chips, carriers, wafers and various other interconnect devices. The term "through hole vias" or "through holes", as used in the present invention, encompasses all kinds of through hole vias and includes so-called "through silicon vias" in silicon wafers.

[0018] Another application wherein the solution can be used with beneficial effects is metallization of smooth, substrates made from glass, ceramic or plastics, preferably with a large surface area. Examples are any kind of displays, as for example any kind of TFT-displays and liquid crystal displays (LCD). As mentioned above, a low roughness of copper surfaces can be reached with the solution of the invention. This effect is advantageous particularly for display applications since a copper layer can be produced with a good conductivity.

[0019] The electroless copper plating solution of the invention can be beneficially used for deposition of copper on a glass substrate, particularly with large surface area, such as glass panels. Glass substrates are used, without limitation, for display applications, as mentioned above. Wet electroless copper deposition, with a solution as mentioned above, on a glass substrate is beneficial in comparison to metal sputtering processes that have been used so far. Benefits that can be reached with wet electroless deposition in comparison to sputtering techniques are, inter alia, reduced internal stress and reduced bending of a glass substrate, reduced equipment maintenance, effective use of metal, reduced material waste, reduced process temperature.

[0020] Further, the electroless copper plating solution of the invention can be beneficially used for plating of glass substrates, particularly glass panels for displays.

[0021] Anyhow, common wet electroless deposition usually produces rougher metal surfaces than sputtering processes. In the case of display production this causes poor switching properties, especially unfavorable prolonged switching times. Thus, for display production it is necessary to generate metal layers with a roughness in the range achieved by sputtering processes. Surprisingly the electroless copper plating solution of the invention is not only able to generate metal layers at higher deposition rate, but simultaneously with a low roughness in a range achieved by sputtering processes.

[0022] Moreover, substrates for display production are activated by metal seed layers for subsequent deposition of metal layers in order to build necessary circuitry and switching elements. Thus, the metal seed layers already display the future pattern of circuitry and switching elements that comprise small and/or isolated activated areas as well as a combination of small and larger activated areas. A high copper deposition rate on glass substrate is reached with the solution of the invention, especially on glass substrates that have these small and/or isolated activated areas. In addition the solution of the invention also is able to deposit metal layers with uniform thickness simultaneously onto small and larger activated areas at high deposition rates.

[0023] 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.

[0024] The solution of the present invention may be prepared by dissolving all components in aqueous liquid medium, preferably in water.

[0025] The solution contains a copper ion source, which may for example be any water soluble copper salt. Copper may for example, and without limitation, be added as copper sulphate, copper chloride, copper nitrate, copper acetate, copper methane sulfonate ($(CH_3O_3S)_2Cu$), copper hydroxide; or hydrates thereof.

[0026] The reducing agent serves for reducing the copper ions in order to obtain metallic copper for plating. Reducing agents that can be employed are for example, and without limitation, formaldehyde, glyoxylic acid, hypophosphite, hydrazine, and borohydride. Preferred reducing agents are formaldehyde and glyoxylic acid.

[0027] 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 converted to the reducing agent. An example is given below with respect to glyoxylic acid.

[0028] A particularly preferred reducing agent is glyoxylic acid because of safety, health and environmental requirements. Even though formaldehyde is a very important and established reducing agent of the common electroless copper plating process, it was classified as a probable human carcinogen. Thus, the electroless aqueous copper plating solution in one embodiment comprises glyoxylic acid or a source of glyoxylic acid. In this embodiment, the solution of the invention does not contain formaldehyde, or, in other words, the solution is according to this embodiment free of formaldehyde.

[0029] 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 dichloro acetic 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.

[0030] In addition to one of the above-mentioned reducing agents, one or more additional reducing agents may be added, as for example hypophosphoric acid, glycolic acid or formic acid, or salts of aforementioned acids. The additional reducing agent is preferably an agent that acts as reducing agent but cannot be used as the sole reducing agent (cf. for example the disclosure in US 7,220,296, col. 4, l. 20-43 and 54-62). Therefore, such additional reducing agent is in this sense also called an "enhancer".

[0031] Electroless copper baths using reducing agents described above preferably employ a relatively high pH, usually between 11 and 14, preferably between 12.5 and 13.5, and are adjusted generally by potassium hydroxide (KOH), sodium hydroxide (NaOH), lithium hydroxide (LiOH), ammonium hydroxide or quarternary ammonium hydroxide, such as tetramethylammonium hydroxide (TMAH). 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.

[0032] Preferred is the use of potassium hydroxide. Potassium hydroxide is of advantage, if glyoxylic acid is used as the reducing agent, because the solubility of potassium oxalate is high. Oxalate anions are formed in the solution by the oxidation of the glyoxylic acid. Thus, potassium hydroxide is especially preferable for stability of the solution of the present invention.

[0033] The solution of the present invention further comprises a mixture of the complexing agent i) Quadrol or a salt thereof with the complexing agent ii) HEDTA or a salt thereof. The mixture of the complexing agent i) Quadrol or a salt thereof with the complexing agent ii) HEDTA or a salt thereof may further comprise the complexing agent iii) EDTA or a salt thereof. The addition of Quadrol or a salt thereof to complexing agent ii) or to a mixture of complexing agent ii) and complexing agent iii) results in an efficient increase in copper deposition. Before the present invention was made, it had been observed that increase of metal deposition rate leads to increased roughness of metal surfaces. In the present invention a high copper deposition rate and a copper surface with low roughness are obtained, surprisingly.

The salts of Quadrol, HEDTA or EDTA may be any suitable, water soluble salts. The counterions of the salts of Quadrol, HEDTA or EDTA are preferably selected from alkali metal ions, earth alkali metal ions and ammonium ions. The counterions of the salts of Quadrol, HEDTA or EDTA are more preferably selected from lithium ions, sodium ions, potassium ions, magnesium ions, calcium ions and ammonium ions.

The solution of the present invention is free of toxic co-metals. The solution of the present invention is especially free of nickel. Nickel forms a more stable complex with the complexing agents used herein than copper. It therefore reduces copper complexation and negatively affects or impedes copper deposition. Moreover, the presence of nickel in the bath would lead to unwanted nickel deposition, which has to be avoided especially in display production.

[0034] In the solution of the present invention, the molar ratio of the complexing agents, related to the total molar amount of all complexing agents, to copper ions is in the range of 1:1 to 10:1, preferably 1:1 to 8:1, more preferably 2:1 to 8:1, even more preferably 2:1 to 5:1, still even more preferably 1.5:1 to 4:1, most preferably 2:1 to 4:1. The molar ratio of the complexing agents, related to the total molar amount of all complexing agents, to copper ions is defined as the ratio of the total molar amount of all complexing agents to the molar amount of copper ions. The total molar amount of all complexing agents is the sum of the individual molar amounts of all complexing agents. "All complexing agents" may be a mixture of complexing agent i) and complexing agent ii) or may be a mixture of complexing agent i), complexing agent ii) and complexing agent iii). In the examples the amount of complexing agents is also given as equivalents. One equivalent is the amount of a complexing agent which completely complexes a given amount of copper ions. In the case of Quadrol, EDTA and HEDTA or a salt thereof one equivalent of complexing agent corresponds to a molar ratio of complexing agent to copper ions of 1:1. In the case of Quadrol, EDTA and HEDTA a molar ratio of 1:1 to 10:1 of complexing agent(s) to copper ions means 1 to 10 equivalents of complexing agent(s) related to copper.

Less complexing agent leads to instability of the bath or deposition does not start. More complexing agent in relation to copper leads to a high density of the bath, which also leads to reduced lifetime and instability of the bath. Using these ranges leads to a beneficial combination of high copper deposition rate and low roughness.

In another embodiment, the molar ratio of the complexing agents, related to the total molar amount of all complexing agents, to copper ions is in the range of 3:1 to 8:1, more preferably 3:1 to 5:1, even more preferably 3:1 to 4:1. Using these ranges leads to a particularly beneficial combination of high copper deposition rate and low roughness. A very reproducible performance, a very reproducible copper deposition, and copper layers with very uniform thickness can be obtained.

[0035] In one embodiment, the ratio of the molar amount of complexing agent i) to the molar amount of complexing agent ii) ranges from 1:0.05 to 1:20, preferably from 1:0.1 to 1:10, more preferably from 1:1 to 1:5, even more preferably from 1:1 to 1:4, most preferably from 1:2 to 1:4. The ratio of the molar amount of complexing agent i) to the molar amount of a mixture of complexing agent ii) and complexing agent iii) (complexing agent i) : [complexing agent ii) + complexing agent iii)]) ranges from 1:0.05 to 1:20, preferably from 1:0.1 to 1:10, more preferably from 1:1 to 1:5, even more preferably from 1:1 to 1:4, most preferably from 1:2 to 1:4.

[0036] The molar amount of a mixture of complexing agent ii) and complexing agent iii) ([complexing agent ii) + complexing agent iii)]) is the sum of the individual molar amounts of complexing agent ii) and complexing agent iii).

[0037] In another embodiment, the ratio of the molar amount of complexing agent i) to the molar amount of complexing agent ii) ranges from 1:0.05 to 1:5, preferably from 1:0.05 to 1:3, more preferably from 1:0.1 to 1:2. The ratio of the molar amount of complexing agent i) to the molar amount of a mixture of complexing agent ii) and complexing agent iii) (complexing agent i) : [complexing agent ii) + complexing agent iii)]) ranges from 1:0.05 to 1:5, preferably from 1:0.05 to 1:3, more preferably from 1:0.1 to 1:2.

[0038] In another embodiment, the ratio of the molar amount of complexing agent i) to the molar amount of complexing agent ii) ranges from 1:5 to 1:20, preferably from 1:7 to 1:15, more preferably from 1:7 to 1:10. The ratio of the molar amount of complexing agent i) to the molar amount of a mixture of complexing agent ii) and complexing agent iii) (complexing agent i) : [complexing agent ii) + complexing agent iii)]) ranges from :5 to 1:20, preferably from 1:7 to 1:15, more preferably from 1:7 to 1:10.

[0039] Using the ranges outlined above leads to a beneficial combination of high copper deposition rate and low roughness.

[0040] According to the invention, the electroless aqueous copper plating solution comprises, as complexing agents, a combination of

i) N,N,N',N'-Tetrakis (2-hydroxypropyl)ethylenediamine (Quadrol) or a salt thereof, and
ii) N'-(2-Hydroxyethyl)-ethylenediamine-N,N,N'-triacetic acid (HEDTA) or a salt thereof.

[0041] In a further embodiment, the electroless aqueous copper plating solution comprises, as complexing agents, a combination of

i) N,N,N',N'-Tetrakis (2-hydroxypropyl)ethylenediamine (Quadrol) or a salt thereof,
ii) N'-(2-Hydroxyethyl)-ethylenediamine-N,N,N'-triacetic acid (HEDTA) or a salt thereof, and
iii) ethylenediamine tetraacetic acid (EDTA) or a salt thereof.

The solution of the invention in one embodiment contains following kinds of ingredients in following concentrations:

Copper ions: 1-5 g/l, corresponding to 0.016-0.079 mol/l, preferably 2.0 - 3.0 g/l
Reducing agent: 0.027-0.270 mol/l, preferably glyoxylic acid: 2-20 g/l, or formaldehyde: 0.8 - 8.5 g/l.

Complexing agents (total amount of all complexing agents): 5-50 g/l, preferably 20 - 40 g/l, more preferably 20 - 30 g/l. The solution of the present invention may comprise - and does not necessarily comprise - further components, as for example stabilizers, surfactants, additives, as rate controlling additives, grain refining additives, pH buffers, pH adjusters, and enhancers. Such further components are for example described in following documents: US 4,617,205 (particularly disclosure in col. 6, l. 17 - col. 7, l. 25), US 7,220,296 (particularly col. 4, l. 63 - col. 6, l. 26), US 2008/0223253 (cf. particularly paragraphs 0033 and 0038).

[0042] Stabilizing agents, also referred to as stabilizers, are compounds that stabilize the electroless plating solution against unwanted outplating in the bulk solution. The term "outplating" means unwanted and/or uncontrolled deposition of copper, for example on the bottom of a reaction vessel or on other surfaces. Stabilizing function can for example be accomplished by substances acting as catalyst poison (for example sulfur or other chalcogenide containing compounds) or by compounds forming copper(I)-complexes, thus inhibiting the formation of copper(I)oxide.

[0043] The solution of the present invention may comprise one or more of a stabilizing agent. Suitable stabilizers are, without limitation, dipyridyls (2,2'-dipyridyl, 4,4'dipyridyl), phenanthroline, mercapto-benzothiazole, thio-urea or its derivatives, cyanides like NaCN, KCN, $K_4[Fe(CN)_6]$; $Na_2S_2O_3$, $K_2S_2O_3$, thiocyanates, iodides, ethanolamines, polymers like polyacrylamides, polyacrylates, polyethylene glycols, or polypropylene glycols and their copolymers.

[0044] In another aspect, the present invention relates to a method for electroless copper plating, the method comprising contacting a substrate with an electroless copper plating solution as described above.

[0045] For example, the substrate may be dipped or immersed in the solution of the invention. In the method a whole surface of a substrate may be plated with copper, or only selected portions.

[0046] It is preferred that the solution be agitated during use. In particular, work- and/or solution-agitation may be used.

[0047] The method will be carried out for a sufficient time to yield a deposit of the thickness required, which in turn will depend on the particular application.

[0048] 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.

[0049] The method of the invention may be useful in providing electroless copper deposits with a thickness in the range of 0.05 μm to 10 μm, preferably between 0.1 μm - 10 μm, 0.1 μm - 5 μm, 0.5 μm - 3 μm. The thickness of copper layer is determined with white light interferometry, as described in the examples.

[0050] The method of the invention produces copper layers on the substrate with a roughness, expressed as the root-mean-square roughness parameter, of 5nm to 60 nm, preferably 5nm - 55nm and more preferably 10nm - 45nm. The obtained roughness is lower by 30 % to 60 %, preferably by 40 % to 50 %, than a method using complexing agent ii) only or using complexing agent iii) only or using a mixture of complexing agents ii) and iii) only. In this case the term "only" means: without addition of Quadrol. The roughness of the copper layer is determined with white light interferometry, as described in the examples.

[0051] Substrates that are generally used for printed circuit board manufacture are most frequently epoxy resins or epoxy glass composites. But other substances, notably phenolic resins, polytetrafluoroethylene (PTFE), polyimides, polyphenyleneoxides, BT(bismaleintriazine)-resins, cyanate esters and polysulphones can be used.

[0052] Aside from the application of the method in the production of printed circuit boards, it may be found to be useful in plating substrates made from glass, ceramic or plastics, as for example ABS, polycarbonate, polyimide or polyethylene terephthalate.

[0053] In another embodiment of the method, the substrate is a substrate made from glass, ceramic or plastics, preferably with a large surface area. A large surface area, means preferably an area of at least one m^2, preferably at least 3 m^2, more preferably at least 5 m^2. A large surface area means in another embodiment preferably an area of 1 m^2 to 9 m^2, more preferably 3 m^2 to 9 m^2, even more preferably 3 m^2 to 6 m^2, still more preferably 5 m^2 to 6 m^2. The substrate has preferably a smooth surface. The term smooth means preferably a roughness (Sq or RMS) of a few nanometers. Preferably the roughness is 5 - 30 nm, measured as RMS. Explanations of the method for roughness measurement and the terms "Sq" and "RMS" are given in the examples.

[0054] In a special embodiment, the substrate is a glass substrate, preferably a glass panel. Said glass substrates, especially glass panels can be used for application in TFT displays, such as liquid crystal displays. Thus, the glass substrate is particularly such one that fulfils the specifications as used in display production, as for example thickness and smoothness. A preferred glass is free from alkali, such as alkali free boro-silicate-glass.

[0055] Glass substrates may be pretreated before the method of the invention is carried out, for example with metal seeds, as further explained below.

[0056] In one embodiment of the method of the present invention, the method is carried out at a temperature in the range of 20 - 60°C, preferably 30 - 55°C. It has been shown in the present invention that when Quadrol is used as complexing agent, in combination with another complexing agent, copper deposition can be done at lower temperatures than in absence of this component. Even though the temperature is lower, the deposition rate is higher than with a bath that does not contain Quadrol.

[0057] The substrate, i.e. the surfaces of the substrate that are to be plated with copper, particularly non-metallic surfaces, may be pretreated by means within the skill in the art (as for example described in US 4,617,205, col 8) to make it/them more receptive or autocatalytic for copper deposition. All or selected portions of a surface may be pretreated. A pretreatment is, however, not necessary in every case and depends on the kind of substrate and surface. Within the pretreatment, it is possible to sensitise substrates prior to the deposition of electroless copper on them. This may be achieved by the adsorption of a catalysing metal (such as a noble metal, for example palladium) onto the surface of the substrate.

[0058] A pretreatment process strongly depends on parameters such as the substrate, the desired application, and the desired properties of the copper surface.

[0059] An exemplary and non-limiting pretreatment process, especially for printing circuit board laminates and other suitable substrates, 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. 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 catalysing 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 catalysing 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 catalysing metal,
f) contacting with an accelerator, wherein components of the colloid, for example a protective colloid, is removed from the catalysing metal.

[0060] In another kind of pretreatment process a permanganate etching step is 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.

[0061] The desmear process may be combined with the above described steps. 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.

[0062] In a pretreatment process which is particularly suitable in metallization for display applications and in metallization of glass substrates, a surface is only contacted with a pre-dip solution and an activator solution and then with the solution of the invention. Contacting with a cleaning solution and an adhesion enhancer before the pre-dip step are optional steps that can be carried out in advance.

[0063] 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 catalysing metal, such as a noble metal, preferably palladium, causing the surface to become catalytic. The ionic catalysing metal is reduced onto the surface by the seed metal.

[0064] 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.

[0065] The exemplary pretreatment processes, or single steps thereof, may be combined to alternative pretreatment processes, if found necessary.

[0066] In a further aspect, the present invention relates to the use of the electroless copper plating solution as described above for the plating of printed circuit boards, wafers, Integrated circuit substrates, molded interconnect device (MID) components, displays, such as liquid crystal or plasma displays, particularly displays for electronic devices or TVs, display components, or plastic parts, such as plastic parts for functional or decorative purposes.

DESCRIPTION OF FIGURES

[0067]

Fig. 1	Effect of a combination of Quadrol with the further complexing agent EDTA on copper thickness and roughness in a plating process
Fig. 2	Effect of a combination of Quadrol with the further complexing agent HEDTA on copper thickness and roughness in a plating process

[0068] 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.

Method of roughness measurement:

[0069] An Optical profilometer / White light interferometer, Model MIC - 520, of ATOS GmbH (Germany) was used to measure the thickness (Height difference between base plane and plated pattern) and surface roughness of electrolessly plated copper layers. White light interferometry is an optical microscopy method known to persons skilled in the art which projects the target area of a sample onto a CCD camera. Using interference objectives equipped with an internal beam splitter, a high-precision reference mirror is projected onto the CCD camera as well. Due to the overlay of both images, a spatially resolved interferogram is created which reflects the height differences between the very flat reference mirror and the sample of interest. In order to image samples with large height distribution a vertical scan scheme is used, i.e. interferograms of the area of interest are imaged as a series within a range of different sample-objective distances. From these data a full three dimensional image is compiled. Using this method, topographic images in the range of 60 μm x 60 μm to 1.2 mm x 1.2 mm can be recorded with a vertical resolution in the range of a few nm.

[0070] The topographic data are used to calculate surface roughness expressed as the root-mean-square roughness parameter, abbreviated as Rq or RMS on surface profiles (profile roughness parameter) and abbreviated as Sq on surface topographies (areal roughness parameter). The meaning of Rq is identical to the meaning of RMS. Rq has the meaning as defined in DIN EN ISO 4287 (German and English version of 1998, Chapter 4.2.2) and Sq has the meaning as defined in ISO 25178-2 of April 2012 (Chapter 4.1.1).

[0071] In addition the topographic data are used to calculate the thickness of the plated copper layers as height difference between the substrate surface (base plane) and the surface of the plated metal pattern. For calculating topographic images, layer thickness and surface roughness the Optical profilometer / White light interferometer, Model MIC - 520, of ATOS GmbH (Germany) was equipped with the computer software Micromap 123, version 4.0, by Micromap Corporation.

[0072] The mode of measurement was Focus 560 M. The topographic images were measured with an objective lens with 10 times magnification and an ocular with 2 times magnification. The topographic images were recorded in the range of 312 μm x 312 μm and consist of 480 x 480 points.

EXAMPLE 1: Combination of Quadrol with a further complexing agent

[0073] Substrate: Alkali-free borosilicate glass, thickness 0.7mm, sputtered seed layer of copper. Pre treatment:

1. alkaline cleaner 40°C/1min
2. rinsing with H_2O
3. sulfuric acid pre dip solution, room temperature (RT)/20sec
4. ionic Pd-activator (exchange-reaction between Cu and Pd) RT/2min
5. rinsing with H_2O

[0074] Electroless copper plating solutions were manufactured. As complexing agents combinations of Quadrol/EDTA (comparative example) and Quadrol/HEDTA (inventive example) were employed. Quadrol was added in amounts of 0 g/l, 2.7 g/l and 5.4 g/l, respectively. Cu^{2+} ions were added as $CuSO_4*6H_2O$. The pH of the baths was 13.2 at 21 °C.

[0075] Substrates were contacted with the respective plating solutions as described above at 45°C for 12 min each. The samples of deposited Cu layers were analysed according to the described method in measuring mode "Focus 560 M". The results are shown in the following tables 1 and 2. Figures 1 and 2 show a chart of the results obtained.

Table 1: Combination of Quadrol/EDTA

Sample No.	1 (comparative)	2 (comparative)	3 (comparative)
EDTA	14.0 g/l	14.0 g/l	14.0 g/l
EDTA in Equivalents	1.5	1.5	1.5
Quadrol	0 g/l	2.7 g/l	5.4 g/l
Quadrol in Equivalents	0	1.1	2.3
Quadrol % vol.	0	10	20
Cu^{2+}	2.0 g/l	2.0g/l	2.0 g/l
KOH	8 g/l	8 g/l	8 g/l
Formaldehyde	4.7 g/l	4.7 g/l	4.7 g/l
2,2'-Dipyridyl	1 mg/l	1 mg/l	1 mg/l
Temperature [°C]	45	45	45
Dwell Time [min]	12	12	12
Cu Thickness [μm]	0.63	0.78	0.78
Sq [nm]	71	51	35

Table 2: Combination of Quadrol/HEDTA

Sample No.	4 (comparative)	5 (inventive)	6 (inventive)
HEDTA	17.1 g/l	17.1 g/l	17.1 g/l
HEDTA in Equivalents	1.9	1.9	1.9
Quadrol	0 g/l	2.7 g/l	5.4 g/l
Quadrol in Equivalents	0	1.1	2.3

(continued)

Sample No.	4 (comparative)	5 (inventive)	6 (inventive)
Quadrol % vol.	0	10	20
Cu^{2+}	2.0 g/l	2.0g/l	2.0g/l
KOH	8 g/l	8 g/l	8 g/l
Formaldehyde	4.7 g/l	4.7 g/l	4.7 g/l
2,2'-Dipyridyl	1 mg/l	1 mg/l	1 mg/l
Temperature [°C]	45	45	45
Dwell Time [min]	12	12	12
Cu Thickness [μm]	0.88	1.06	1.07
Sq [nm]	58	54	40

[0076] Dwell time means the time of contacting the substrates with the electroless copper plating solutions.

[0077] A combination of Quadrol/EDTA (table 1, Fig. 1) or a combination of Quadrol/HEDTA (table 2, Fig. 2) leads to increased copper thicknesses in comparison to EDTA alone or HEDTA alone, respectively, when the same process time is chosen. The results show that addition of Quadrol increases the deposition rate while significantly reducing the roughness of the deposited copper layers. If Quadrol is added to a solution already containing HEDTA the roughness in relation to the deposition rate is lower than if Quadrol is added to a solution already containing EDTA alone.

EXAMPLE 2: comparative example

[0078] Substrates as used in Example 1 were pre-treated as described in Example 1.
Electroless copper plating solutions were prepared as described in Example 1. The copper plating solutions contained a combination of complexing agents Quadrol and HEDTA in a molar ratio of 1:20. The total molar amount of complexing agents was varied in relation to the molar amount of copper ions as shown in Table 3. As stabilizer a mixture of cyanide and sulphur compounds was added.

[0079] Two pre-treated substrates (sample A and B) were contacted with the respective plating solutions as described above at 45 °C for 10 min each. The samples of deposited Cu layers were analysed as described in Example 1. The results are shown in Table 3.

Table 3: Variation of ratio of complexing agents to copper ions.

Sample No.	7 (comparative)	8 (comparative)
HEDTA in equivalents	0.476	10.48
Quadrol in equivalents	0.024	0.52
Total equivalents of complexing agents	0.5	11
Cu^{2+}	2.5 g/l	2.5 g/l
Cu^{2+} in equivalents	1	1
NaOH	8 g/l	8 g/l
Formaldehyde	4.5 g/l	4.5 g/l
Stabilizer	4 mg/l	4 mg/l
Temperature [°C]	45	45
Dwell Time [min]	10	10
Cu Thickness [μm]		

(continued)

Sample No.	7 (comparative)	8 (comparative)
Sample A	1.25	1.77
Sample B	1.23	1.95
Mean	1.24	1.86
Sq [nm]		
Sample A	93	161
Sample B	104	187
Mean	99	174

[0080] Both electroless copper plating solutions deposited copper with a high deposition rate but the roughness of the copper layers obtained was too high. In addition, when Quadrol and HEDTA were used in a molar ratio to copper ions of 0.5:1, the electroless copper plating solution became instable. When Quadrol and HEDTA were used in a molar ratio to copper ions of 11:1, the deposited copper layers showed wild growth and blistering.

Claims

1. An electroless aqueous copper plating solution, comprising

   - a source of copper ions,
   - a reducing agent or a source of a reducing agent,

   characterized in that the electroless aqueous copper plating solution further comprises a combination comprising

   i) N,N,N',N'-Tetrakis (2-hydroxypropyl)ethylenediamine or a salt thereof, and
   ii) N'-(2-Hydroxyethyl)-ethylenediamine-N,N,N'-triacetic acid or a salt thereof,

   as complexing agents; and
   wherein the ratio of the total molar amount of all complexing agents to copper ions is in the range of 1:1 to 10:1.

2. The electroless aqueous copper plating solution according to claim 1, wherein the combination of complexing agents further comprises

   iii) ethylenediamine tetraacetic acid or a salt thereof.

3. The electroless aqueous copper plating solution according to one of the preceding claims, wherein the ratio of the total molar amount of all complexing agents to copper ions is in the range of 1:1 to 8:1.

4. The electroless aqueous copper plating solution according to one of the preceding claims, wherein the ratio of the molar amount of complexing agent i) to the molar amount of complexing agent ii) ranges from 1:0.05 to 1:20.

5. The electroless aqueous copper plating solution according to claims 2 or 3, wherein the ratio of the molar amount of complexing agent i) to the molar amount of a mixture of complexing agent ii) and complexing agent iii) ranges from 1:0.05 to 1:20.

6. The electroless aqueous copper plating solution according to one of the preceding claims, wherein the reducing agent is selected from glyoxylic acid and formaldehyde.

7. A method for electroless copper plating, the method comprising contacting a substrate with an electroless aqueous copper plating solution according to one of claims 1-6.

8. The method according to claim 7, wherein the substrate is a substrate made from glass, ceramic or plastics.

9. The method according to claim 7 or 8, wherein the substrate is a glass substrate, preferably a glass panel.

10. The method according to claims 7 - 9, wherein the substrate has a large surface area and the large surface area is a surface area of at least 5 m^2.

11. The method according to claims 7 - 10, wherein on the substrate a copper layer with a thickness of 0.5 μm to 3 μm is produced.

12. The method according to claims 7 - 11, wherein on the substrate a copper layer with a roughness, expressed as the root-mean-square roughness parameter, of 5 to 60 nm is produced.

13. The use of an electroless aqueous copper plating solution according to one of claims 1 - 6 for the plating of printed circuit boards, integrated circuit substrates, wafers, molded interconnect devices, displays, display components or plastic parts.

14. The use of an electroless copper plating solution according to one of claims 1 - 6 for the plating of glass substrates, particularly glass panels for displays.

Patentansprüche

1. Stromlose wässrige Verkupferungslösung, umfassend

- eine Quelle für Kupferionen,
- ein Reduktionsmittel oder eine Quelle eines Reduktionsmittels,

dadurch gekennzeichnet, dass die stromlose wässrige Verkupferungslösung ferner eine Kombination umfasst, umfassend

i) N,N,N',N'-Tetrakis(2-hydroxypropyl)ethylen-diamin oder ein Salz davon und
ii) N'-(2-Hydroxyethyl)-ethylendiamin-N,N,N'-tri-essigsäure oder ein Salz davon als Komplexbildner;

und
wobei das Verhältnis der gesamten molaren Menge aller Komplexbildner zu Kupferionen im Bereich von 1:1 bis 10:1 liegt.

2. Stromlose wässrige Verkupferungslösung nach Anspruch 1, wobei die Kombination der Komplexbildner ferner

iii) Ethylendiamintetraessigsäure oder ein Salz davon umfasst.

3. Stromlose wässrige Verkupferungslösung nach einem der vorhergehenden Ansprüche, wobei das Verhältnis der gesamten molaren Menge aller Komplexbildner zu Kupferionen im Bereich von 1:1 bis 8:1 liegt.

4. Stromlose wässrige Verkupferungslösung nach einem der vorhergehenden Ansprüche, wobei das Verhältnis der molaren Menge des Komplexbildners i) zu der molaren Menge g/l Komplexbildner ii) im Bereich von 1:0,05 bis 1:20 liegt.

5. Stromlose wässrige Verkupferungslösung nach den Ansprüchen 2 oder 3, wobei das Verhältnis der molaren Menge des Komplexbildners i) zu der molaren Menge einer Mischung von Komplexbildner ii) und Komplexbildner iii) im Bereich von 1:0,05 bis 1:20 liegt.

6. Stromlose wässrige Verkupferungslösung nach einem der vorhergehenden Ansprüche, wobei das Reduktionsmittel ausgewählt ist aus Glyoxylsäure und Formaldehyd.

7. Verfahren zum stromlosen Verkupfern, wobei das Verfahren das Kontaktieren eines Substrats mit einer stromlosen wässrigen Verkupferungslösung gemäß einem der Ansprüche 1-6 umfasst.

8. Verfahren nach Anspruch 7, wobei das Substrat ein Substrat aus Glas, Keramik oder Kunststoffen ist.

9. Verfahren nach Anspruch 7 oder 8, wobei das Substrat ein Glassubstrat ist, vorzugsweise eine Glasscheibe.

10. Verfahren nach den Ansprüchen 7-9, wobei das Substrat eine große Oberfläche aufweist und die große Oberfläche eine Oberfläche von mindestens 5 m^2 ist.

11. Verfahren nach den Ansprüchen 7-10, wobei auf dem Substrat eine Kupferschicht mit einer Dicke von 0,5 μm bis 3 μm produziert wird.

12. Verfahren nach den Ansprüchen 7-11, wobei auf dem Substrat eine Kupferschicht mit einer Rauheit, ausgedrückt als quadratischer Mittelwert Rauheitsparameter (Rq), von 5 bis 60 nm produziert wird.

13. Verwendung einer stromlosen wässrigen Verkupferungslösung gemäß einem der Ansprüche 1-6 zum Plattieren von gedruckten Schaltplatinen, Substraten für integrierte Schaltkreise, Wafern, spritzgegossenen Schaltungsträgern (Molded Interconnect Devices; MID), Displays, Displaykomponenten oder Kunststoffteilen.

14. Verwendung einer stromlosen Verkupferungslösung gemäß einem der Ansprüche 1-6 zum Plattieren von Glassubstraten, insbesondere Glasscheiben für Displays.

Revendications

1. Solution aqueuse de cuivrage sans courant, comprenant

- une source d'ions cuivre,
- un réducteur ou une source d'un réducteur,

caractérisée en ce que la solution aqueuse de cuivrage sans courant comprend en outre une combinaison comprenant

i) de la N,N,N',N'-tétrakis(2-hydroxypropyl)éthylènediamine ou un sel de celle-ci, et
ii) de l'acide N'-(2-hydroxyéthyl)-éthylènediaminetriacétique ou un sel de celui-ci,

comme agents complexants ; et
dans laquelle le rapport de la quantité molaire totale de tous les agents complexants aux ions cuivre se situe dans la gamme de 1:1 à 10:1.

2. Solution aqueuse de cuivrage sans courant selon la revendication 1, dans laquelle la combinaison d'agents complexants comprend en outre

iii) de l'acide éthylènediamine-tétraacétique ou un sel de celui-ci.

3. Solution aqueuse de cuivrage sans courant selon une des revendications précédentes, dans laquelle le rapport de la quantité molaire totale de tous les agents complexants aux ions cuivre se situe dans la gamme de 1:1 à 8:1.

4. Solution aqueuse de cuivrage sans courant selon une des revendications précédentes, dans laquelle le rapport de la quantité molaire d'agent complexant i) à la quantité molaire d'agent complexant ii) va de 1:0,05 à 1:20.

5. Solution aqueuse de cuivrage sans courant selon les revendications 2 ou 3, dans laquelle le rapport de la quantité molaire d'agent complexant i) à la quantité molaire d'un mélange d'agent complexant ii) et d'agent complexant iii) va de 1:0,05 à 1:20.

6. Solution aqueuse de cuivrage sans courant selon une des revendications précédentes, dans laquelle le réducteur est choisi entre l'acide glyoxylique et le formaldéhyde.

7. Procédé de cuivrage sans courant, le procédé comprenant la mise en contact d'un substrat avec une solution aqueuse de cuivrage sans courant selon une des revendications 1 à 6.

8. Procédé selon la revendication 7, dans lequel le substrat est un substrat fabriqué à partir de verre, de céramique ou de plastique.

9. Procédé selon la revendication 7 ou 8, dans lequel le substrat est un substrat de verre, de préférence un panneau de verre.

10. Procédé selon les revendications 7 à 9, dans lequel le substrat a une grande surface et la grande surface est une surface d'au moins 5 m^2.

11. Procédé selon les revendications 7 à 10, dans lequel une couche de cuivre avec une épaisseur de 0,5 µm à 3 µm est produite sur le substrat.

12. Procédé selon les revendications 7 à 11, dans lequel une couche de cuivre avec une rugosité exprimée comme le paramètre de rugosité moyenne quadratique de 5 à 60 nm est produite sur le substrat.

13. Utilisation d'une solution aqueuse de cuivrage sans courant selon une des revendications 1 à 6 pour le revêtement de cartes de circuits imprimés, de substrats de circuits intégrés, de tranches, de dispositifs d'interconnexion moulés, d'écrans, de composants d'écrans ou de pièces en plastique.

14. Utilisation d'une solution de cuivrage sans courant selon une des revendications 1 à 6 pour le revêtement de substrats de verre, en particulier de panneaux de verre pour écrans.

Figure 1

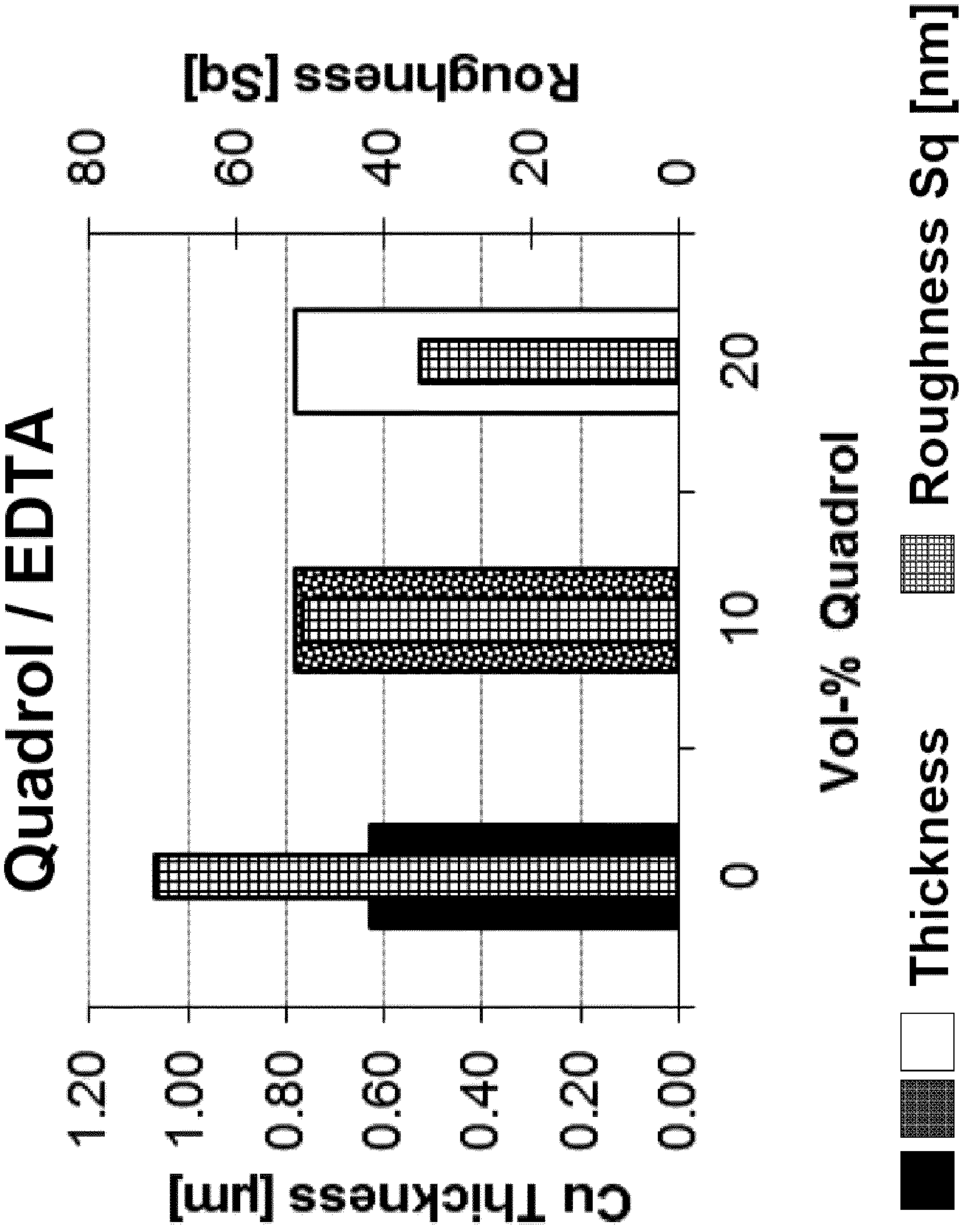
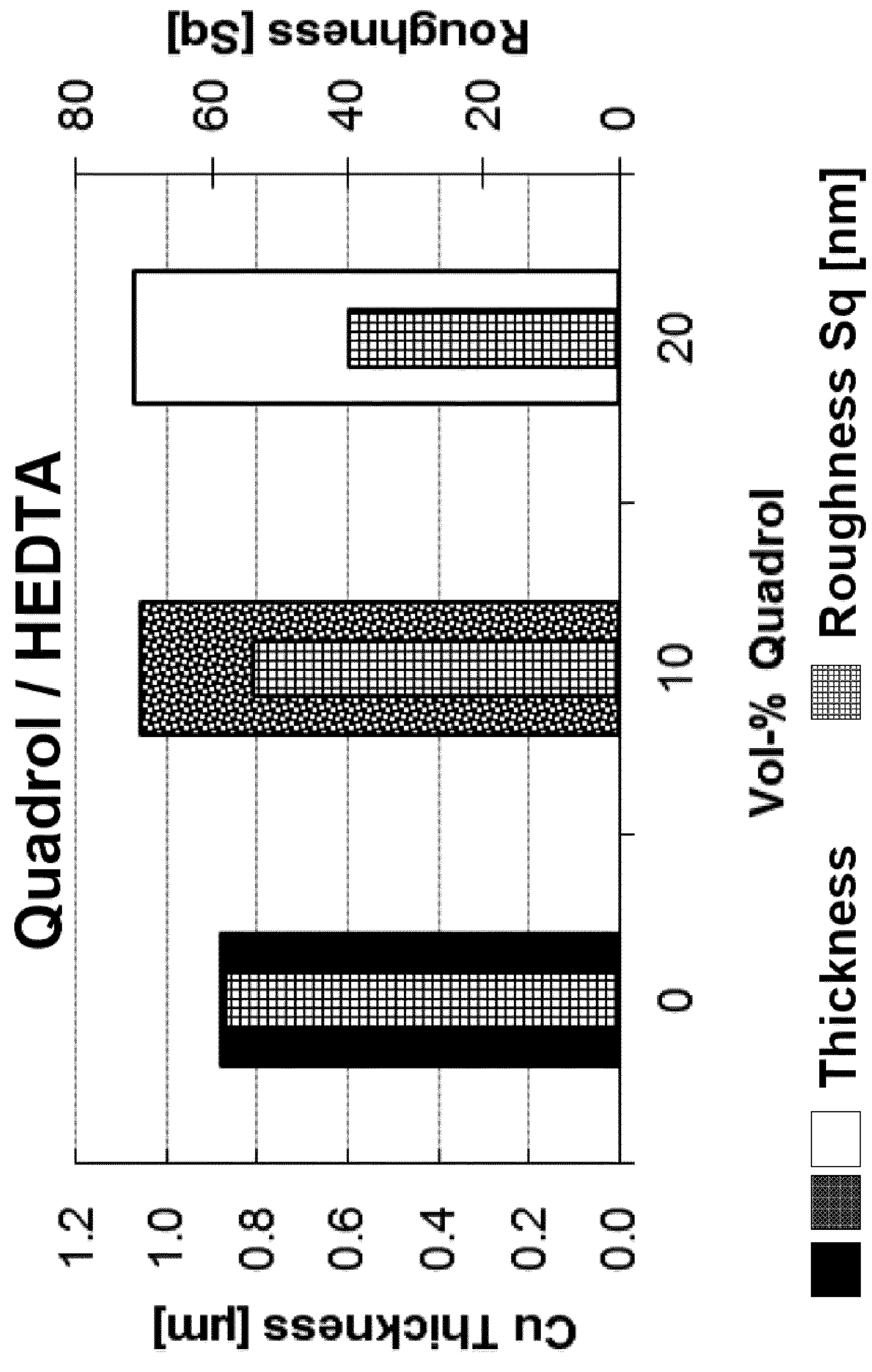

Quadrol / EDTA
Cu Thickness [µm]
1.20
1.00
0.80
0.60
0.40
0.20
0.00
Roughness [Sq]
80
60
40
20
0
0
10
20
Vol-% Quadrol
Thickness
Roughness Sq [nm]

Figure 2


Quadrol / HEDTA
Cu Thickness [µm]
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Roughness [Sq]
80
60
40
20
0
0
10
20
Vol-% Quadrol
Thickness
Roughness Sq [nm]

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

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