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(54) **METHOD FOR PROMOTING ADHESION BETWEEN DIELECTRIC SUBSTRATES AND METAL LAYERS**

VERFAHREN ZUR FÖRDERUNG DER HAFTUNG ZWISCHEN DIELEKTRISCHEN SUBSTRATEN UND METALLSCHICHTEN

PROCÉDÉ PERMETTANT DE FAVORISER L'ADHÉRENCE ENTRE DES SUBSTRATS DIÉLECTRIQUES ET DES COUCHES MÉTALLIQUES

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Description

Field of the Invention

[0001] The present invention relates to novel processes for metallization of dielectric, substrate surfaces applying silane compositions. The method results in metal plated surfaces exhibiting high adhesion between the substrate and the plated metal while at the same time leaving the smooth substrate surface intact.

Background of the Invention

[0002] Various methods are known of metallizing dielectric substrate surfaces. In wet chemical methods, the surfaces to be metallised are, after an appropriate preliminary treatment, either firstly catalysed and then metallised in an electroless manner and thereafter, if necessary, metallised electrolytically, or are directly electrolytically metallised.

[0003] In EP 0 616 053 A1 there is disclosed a method for direct metallisation of dielectric substrate surfaces, in which the surfaces are firstly treated with a cleaner / conditioner solution, thereafter with an activator solution, for example a palladium colloidal solution, stabilised with tin compounds, and are then treated with a solution which contains compounds of a metal which is more noble than tin, as well as an alkali hydroxide and a complex former. Thereafter the surfaces can be treated in a solution containing a reducing agent, and can finally be electrolytically metallised.

[0004] WO 96/29452 concerns a process for the selective or partial electrolytic metallisation of surfaces of substrates made from electrically non-conducting i.e. dielectric materials which for the purpose of the coating process are secured to plastic-coated holding elements. The proposed process involves the following steps: a) preliminary treatment of the surfaces with an etching solution containing chromium (VI) oxide; followed immediately by b) treatment of the surfaces with a colloidal acidic solution of palladium-/tin compounds, care being taken to prevent prior contact with adsorption-promoting solutions; c) treatment of the surfaces with a solution containing a soluble metal compound capable of being reduced by tin (II) compounds, an alkali or alkaline earth metal hydroxide, and a complex forming agent for the metal in a quantity sufficient at least to prevent precipitation of metal hydroxides; d) treatment of the surfaces with an electrolytic metallisation solution. Such method is particularly suitable for ABS (acryl-butadience styrole) and ABS/PC (polycarbonate) based plastic substrates.

[0005] Alternatively, conductive polymers can be formed on the dielectric substrate surface to provide a first conductive layer for subsequent metal plating of the surface.

[0006] US 2004/0112755 A1 describes direct electrolytic metallization of electrically non-conducting substrate surfaces comprising bringing the substrate surfaces into contact with a water-soluble polymer, e.g. a thiophene; treating the substrate surfaces with a permanganate solution; treating the substrate surfaces with an acidic aqueous solution or an acidic microemulsion of aqueous base containing at least one thiophene compound and at least one alkane sulfonic acid selected from the group comprising methane sulfonic acid, ethane sulfonic acid and ethane disulfonic acid; electrolytically metallizing the substrate surfaces.

[0007] US 5,693,209 is directed to a process for directly metallizing a circuit board having nonconductor surfaces, includes reacting the nonconductor surface with an alkaline permanganate solution to form manganese dioxide chemically adsorbed on the nonconductor surface; forming an aqueous solution of a weak acid and of pyrrole or a pyrrole derivative and soluble oligomers thereof; contacting the aqueous solution containing the pyrrole monomer and its oligomers with the nonconductor surface having the manganese dioxide adsorbed chemically thereon to deposit an adherent, electrically conducting, insoluble polymer product on the nonconductor surface; and directly electrodepositing metal on the nonconductor surface having the insoluble adherent polymer product formed thereon. The oligomers are advantageously formed in aqueous solution containing 0.1 to 200 g/l of the pyrrole monomer at a temperature between room temperature and the freezing point of the solution.

[0008] US 4,976,990 relates to the metallization of dielectric substrate surfaces, particularly to the electroless metallization of dielectric through-hole surfaces in double-sided or multi-layer printed circuit boards. The methods involves roughening the surface and subsequently applying a silane composition to such treated surface. Substantial roughening of the surface occurs if the process is performed in this sequence of treatment steps. The method disclosed in this patent includes a micro etching solution used to remove oxide films from the metal foil, lines 61 to 65. The method, however, is not suitable to obtain a good adhesion between the substrate material and a subsequently plated metal layer according to a method of the present invention.

[0009] A similar method is disclosed in WO 88/02412.

[0010] EP 0 322 233 A2 relates to a method for producing ultrafine patterns of silver metal films on substrates employing application of a polymerisable silane, diborane containing solutions, etching in solutions containing sodium hydroxide and hydrogen peroxide and finally applying the silver metal layer. Such method is not suitable to produce an adherent metal film to a substrate according to the method of the present invention.

[0011] All methods described require substantial roughening of the surface of the nonconductive, dielectric substrate

prior to metallization to ensure sufficient adhesion between the substrate and the plated metal layer. Roughening has generally been considered indispensable because it is used to prepare the surface of the dielectric substrate. This is because roughening has been considered requisite to achieve good adhesion between the substrate and the metal layer.

[0012] However, a rough surface imparts the functionality of the metal plated surface, e.g with regards to its use as conductor lines in electronics applications.

[0013] The ongoing miniaturization of features of HDI printed circuit boards, IC substrates and the like requires more advanced manufacturing methods than conventional methods such as formation of circuitry by a print and etch method. Such features require that the surface of the substrate is roughened to a limited degree only.

Summary of the Invention

[0014] Thus, it is an object of the present invention to provide a method for metallization of dielectric substrate surfaces without substantially roughening the surface while still obtaining a high adhesion between the substrate and the metal layer.

[0015] This object is achieved by a method for treating a surface of a dielectric substrate to prepare said surface for subsequent wet chemical metal plating, such method comprising in this order the steps of

(i) treating said surface with a solution comprising at least one organosilane compound;

(ii) treating said surface with a solution comprising an oxidizing agent selected from aqueous acidic or alkaline solutions of permanganate. and followed by

(iii) metallizing the substrate after step (ii) with a wet chemical plating method.

Brief Description of the Drawings

[0016]

Fig. 1 shows a method for manufacture of fine line circuitry known in the art as semi-additive process (SAP).

Fig, 2 shows a surface after permanganate treatment of GX92 substrate material according to example P12.

Fig. 3 shows a surface after permanganate treatment of GX92 substrate material treated with an alkaline permanganate solution according to conditions known in the state of the art.

Detailed Description of the Invention

[0017] According to the present invention the substrate is first treated in step (i) with a composition containing an organosilane compound.

[0018] The organosilane compound is applied as a solution, preferably a solution of an organic solvent having a high boiling point, preferably in the range of 60 to 250 °C and more preferred in the range of 80 to 200 °C. Organic solvents within the meaning of this invention are polar organic solvents suitable to dissolve silane compounds.

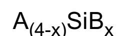
[0019] Suitable organic solvents comprise alcohols, ethers, amines, and acetates. Examples are ethanol, 2-propanol, tetrahydrofuran, ethylene glycol, diethyleneglycol, 2-isopropoxyethanol (IPPE), di(propyleneglycol)methyletheracetate (DPGMEA), 2-ethyl-1-hexanol, glycerine, dioxin, butyrolacton, N-methyl pyrrolidone (NMP), dimethyl formamide, dimethylacetamide, ethanolamine, propylene glycol methyl ether acetate (PMA), half ethers and half esters of ethylene glycols.

[0020] The concentration of the organosilane can vary over a wide range depending on the application and the specific organosilane compound. The suitable concentration can be obtained by routine experiments. Suitable concentration generally vary between as low as 0.2 wt.% to 30 wt.%, preferably between 0.5 wt.% to 20 wt.%, even more preferred between 1 wt.% and 8 wt.%.

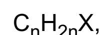
[0021] Contacting the dielectric substrates with a solution containing organosilanes according to method step (i). is performed by dipping or immersing the substrates into said solution; or by spraying the solution to the substrates. Contacting the substrate with a solution containing organosilanes according to method step (i). is performed at least once. Alternatively said contacting can be performed several times, preferably between 2 to 10 times, more preferred between 2 to 5, even more preferred between 1 to 3 times. Most preferred contacting is once to twice.

[0022] Contacting the substrate with a solution containing organosilanes according to method step (i). is performed for a time period ranging from 10 seconds to 20 minutes, preferred from 10 seconds to 10 minutes, most preferred from 10 seconds to 5 minutes.

[0023] Contacting the substrate with a solution containing organosilane according to method step i. is performed at a temperature ranging from 15 to 100 °C, preferred from 20 to 50 °C, most preferred from 23 to 35 °C.
[0024] The organosilane compound is preferably selected from the group represented by the following formula



wherein
each A is independently a hydrolyzable group,
x is 1 to 3, and
each B is independently selected from the group consisting of C_1-C_{20} alkyl, aryl, amino aryl and a functional group represented by the formula



wherein
n is from 0 to 15, preferably 0 to 10 even more preferably 1 to 8, most preferably 1, 2, 3, 4 and
X is selected from the group consisting of amino, amido, hydroxy, alkoxy, halo, mercapto, carboxy, carboxy ester, carboxamide, thiocarboxamide, acyl, vinyl, allyl, styryl, epoxy, epoxycyclohexyl, glycidoxy, isocyanato, thiocyanato, thioisocyanato, ureido, thioureido, guanidino, thioglycidoxy, acryloxy, methacryloxy groups; or X is a residue of a carboxy ester; or X is $Si(OR)_3$, and wherein R is a C_1-C_5 alkyl group.
[0025] Preferably, the hydrolyzable group A is selected from the group consisting of-OH, $-OR^1$ and wherein R^1 is C_1-C_5 alkyl, - $(CH_2)_yOR^2$ and wherein y is 1, 2 or 3 and R^2 is H or C_1-C_5 alkyl, $-OCOR^3$ and and wherein R^3 is H or C_1-C_5 alkyl.
[0026] If B is an alkyl group it is preferably a C_1-C_{10} alkyl, even more preferred C_1-C_5 alkyl group like methyl, ethyl, propyl or isopropyl. Preferred aryl groups are phenyl- and benzyl-groups, either substituted or unsubsituted. A preferred amino aryl group is $-NH(C_6H_5)$.
[0027] Functional groups X within the meaning of this invention can be further functionalized. For example X = amino comprises alkylamine- or arylamine substitued amines like 3-(N-Styrylmethyl-2-aminoethylamino).
[0028] For the functional group X being $Si(OR)_3$, R preferably is methyl, ethyl, propyl or isopropyl.
[0029] Examples of particular classes of compounds within the formulas above are vinylsilanes, aminoalkylsilanes, ureidoalkylsilane esters, epoxyalkylsilanes and methacryloalkylsilane esters, in which the reactive organic functions are, respectively, vinyl, amino, ureido, epoxy and methacryloxy. Examples of the vinylsilanes are vinyltrichlorosilane, vinyltriethoxysilane, vinyltrimethoxysilane, vinyl-tris-(beta(2)-methoxyethoxy) silane and vinyltriacetoxysilane. As examples of the aminoalkylsilanes, which are the preferred organosilanes for use in the present invention, are gamma(3)-aminopropyltriethoxysilane, gammaaminopropyltrimethoxysilane, N-beta-(Aminoethyl)-gamma-aminopropyltrimethoxysilane, and N'-(beta-aminoethyl)-N-(beta-aminoethyl)-gamma-amino-propyltrimethoxysilane. A suitable ureidoalkylsilane ester is gammaureidoal-kyltriethoxysilane, while suitable expoxyalkylsilanes are beta-(3,4-epoxycyclohexyl)-ethyltrimethoxysilane and gammaglycidoxypropyltrimethoxysilane. Useful methacryloxysilane esters are gamma-methacryloxypropyltrimethoxy silane and gamma-methacryloxypropyl-tris-(beta-methoxyethoxy) silane.
[0030] The at least one organosilane compound can either be a monomeric organosilane compound or an oligomeric organosilane compound which is obtained by a (partial) hydrolyzation and condensation of a monomeric organosilane compound according to the present invention prior to the deposition onto the surface of the dielectric substrate.
[0031] The hydrolysis and condensation of organosilane compounds is well known in the art. For example, the monomeric organosilane compound is reacted with an acidic catalyst, for example, acetic acid or diluted hydrochloric acid leading to a clear solution of an oligomeric organosilane compound derived from the monomeric organosilane compound.
[0032] Such oligomeric silanes derived from monomeric organosilane compound according to the present by hydrolization shall be included into the scope of the present invention.
[0033] Optionally, the substrate can be heat treated after method step (i). Such treatment is generally performed at a temperature between 60 - 200 °C, more preferred between 80 - 150 °C. The treatment time can vary, e.g. between 1 and 30 minutes, preferred between 1 and 10 minutes.
[0034] Thereafter, the substrate is treated with a solution comprising an oxidizing agent in step (ii) selected fromaqueous acidic or alkaline solution of permanganate.
[0035] It was a surprisingly found that other oxidising agents than permanganate, for example a mixture of hydrogen peroxide and sulphuric acid or chromic acid are not suitable for a method according to the present invention, since they do not result in sufficient adhesion between the substrate and the subsequently plated metal layer. This was unexpected since the prior art teaches that all oxidising agents essentially result in the same surface modification.
[0036] Alkaline solutions of permanganate, e.g. sodium or potassium permanganate are preferred. The solution preferably contains 20 - 100 g/l permanganate ions and 10 - 40 g/l hydroxide ions. A preferred hydroxide ion source is

sodium or potassium hydroxide.

[0037] Contacting the dielectric substrates with a solution containing an oxidizing agent according to method step (ii) is performed by dipping or immersing the substrates into said solution; or by spraying the solution to the substrates.

[0038] Contacting the substrate with a solution containing an oxidizing agent according to method step (ii) is performed for a time period ranging from 30 seconds to 30 minutes, preferred from 30 seconds to 10 minutes.

[0039] Contacting the substrate with a solution containing an oxidizing agent according to method step (ii) is performed at a temperature ranging from 20 to 95 °C, preferred from 50 to 85 °C.

[0040] In one embodiment of the present invention the method comprises the following steps:

(i) treating said surface with a solution comprising at least one organosilane compound for a period of time of between 10 s and 10 min. at a temperature of between 15 and 50 °C

(ii) treating said surface with a solution comprising an oxidizing agent selected from an alkaline aqueous solution of permanganate ions in a concentration of 20 - 100 g/l for a period of time of between 1 and 30 min. at a temperature of between 20 and 95 °C to obtain a roughened surface having an average surface roughness Ra of less than 150 nm.

[0041] A surface roughness Ra of less than 150 nm can be between 50 and 150 nm, preferably between 60 and 130 nm and even more preferably between 70 and 120 nm.

[0042] Various kinds of dielectric substrates can be metallized with a method according to the present invention. Metallization is performed by a wet chemical plating method. Such plating method comprises electroless, immersion and electrolytic plating processes, usually performed in aqueous solution.

[0043] The dielectric substrates to be metallized can be selected from the group comprising plastics, plastic-glass, and plastic-ceramic composites.

[0044] Plastics can be selected from the group comprising acrylnitrile-butadiene-styrol-copolymer (ABS copolymer); polyamide; a mixture of an ABS copolymer and at least one other polymer which is different to the ABS copolymer; polycarbonate (PC); ABS/PC blends; epoxy resin; bismaleimide-triazine resin (BT); cyanate ester resin; polyimide; polyethylene terephthalate (PET); polybutylene terephthalate (PBT); polylactic acid (PLA); polypropylene (PP); and polyester.

[0045] Also, dielectric substrates used in the manufacture of printed circuit boards can be used. Such material typically consists of epoxy based material, for example epoxy blends like epoxy-benzotriazole blends, epoxy-cyanate-blends, epoxy-propylene blends, or epoxy-polyimide blends.

[0046] For step (iii) several methods for plating a metal onto a substrate by applying a wet-chemical plating method are known to the person skilled in the art. According to the present invention the wet chemical plating method preferably is an electrolytic plating method, an immersion plating process or an electroless plating method.

[0047] Dielectric substrates, e.g. plastic objects can then be metallized after activation by using an electroless metallising method or alternatively by using a direct plating method (electrolytic plating method). The object is first cleaned followed by application of e.g. a noble metal or conductive polymer and then finally metallised.

[0048] A typically activation of dielectric substrates like printed circuit boards for subsequent metal plating is performed as follows:

[0049] Preferably, the first conductive layer comprises copper and is deposited by electroless plating. Preferably in this case, the substrate is activated by e.g., deposition of a noble metal containing colloid or a solution comprising noble metal ions prior to electroless deposition of copper. The most preferable activation is by deposition of palladium-tin colloids or palladium ions. Such methods are established in the arts and known to the skilled person.

[0050] Instead of copper the first conductive layer can comprise nickel.

[0051] An exemplary and non-limiting pretreatment process, especially for printed circuit board laminates and other suitable substrates, may comprise the following steps

a) contacting the substrate with an activator solution, that contains colloidal or ionic catalysing metal, such as a noble metal, preferably palladium, causing the the substrate's surface to become catalytic,
and optionally, particularly if the activator contains ionic catalysing metal,
b) contacting the substrate with a reducer, wherein the metal ions of an ionic activator are reduced to elemental metal,
or, if the activator contains colloidal catalysing metal,
c) contacting the substrate with an accelerator, wherein the components of the colloid, for example a protective colloid, is removed from the catalysing metal.

[0052] The method according to the present invention is particularly suitable for manufacture of fine line circuitry. This is shown in Fig. 1.

[0053] 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 (1) having on at least a portion of the back side a copper area which can be for example a contact area (2), and a second dielectric layer (3) attached to the back side of the dielectric build-up layer (1). Such a substrate is shown in Fig. 1 a. At least one opening (4) such as a blind micro via is formed by e.g. laser drilling in the build-up layer (1) which extends through the substrate to the copper area (2) on the back side of the build-up layer (1) (Fig. 1 b). The dielectric surface of the build-up layer (1) is subjected to a desmear process in the next step which leads to a roughened top surface (5a) of the build-up layer (1) and a roughened surface (5b) of the dielectric side walls of the at least one opening (4) (Fig. 1 c).

[0054] Further activation of the roughened top surface (5a) and the roughened side walls (5b) by e.g. depositing a noble metal containing activator is necessary for successive electroless plating of copper. Next, a conductive seed layer (6), generally made of copper, is deposited by electroless plating onto the roughened top surface (5a) of the build-up layer (1) and the roughened side walls (5b) of the at least one opening (4) (Fig. 1 d). Such a conductive layer (6) usually has a thickness of 0.8 μm to 1.5 μm which is a) required to provide a sufficient electrical conductivity on the roughened top surface (5a) for successive electroplating of copper and b) to ensure that during electroless plating of copper also a sufficient electrical conductivity is provided to the roughened side walls (5b) of the at least one opening (4).

[0055] A thicker layer of copper (8) is then selectively electroplated into openings of a patterned resist layer (7) onto the roughened and activated top surface of the build-up layer (1) and the roughened and activated dielectric walls of the at least one opening (4) (Fig. 1e to f). The patterned resist layer (7) is removed (Fig. 1 g) and those portions of the conductive layer (6) which are not covered by electroplated copper (8) are removed by differential etching (Fig. 1 h). Such a process is for example disclosed in US 6,278,185 B1 and US 6,212,769 B1.

[0056] A method for manufacturing fine line circuitry on a printed circuit board comprises, in this order, the following steps

(i) Providing a substrate comprising a bare dielectric build-up layer (1) having on at least a portion of the back side a contact area (2) and a second dielectric layer (3) attached to the back side of the build-up layer (1),

(ii) Forming at least one opening (4) in the build-up layer (1) which extends through the substrate to the contact area (2),

(iii) Treating said surface with a solution comprising at least one organosilane compound,

(iv) Treating said surface with a solution comprising an oxidizing agent,

(v) Depositing a conductive seed layer (6) onto the top surface (5a) of the dielectric build-up layer (1) and the dielectric side walls (5b) of the at least one opening (4), and

(vi) Selectively depositing a copper layer (8) into openings of a patterned resist layer (7) by electroplating.

[0057] Dielectric substrates, e.g. plastic objects can then be metallized after activation by using an electroless metallising method or alternatively by using a direct plating method (electrolytic plating method). The object is first cleaned followed by application of e.g. a noble metal or conductive polymer and then finally metallised.

[0058] A typically activation of dielectric substrates for subsequent metal plating is performed as follows:

[0059] The plastic is activated for electroless metallisation using an activator which contains a noble metal and then electrolessly metallised. A thicker metal layer can then also be applied electrolytically afterwards. In the case of the direct plating method, the etched surface is usually treated with a palladium colloid solution and then with an alkaline solution which contains copper ions forming a complex with a complexing agent. Thereafter the object can then be electrolytically metallised directly (EP 1 054 081 B1).

[0060] A suitable metallizing sequence in step (iii) would involve the following steps:

A) treatment with a solution of a colloid or with a compound, particularly a salt of a metal of Group VIIIB or IB of the Periodic Table of the Elements (noble metal), particularly a palladium / tin colloid; and

B) electrolytic metallization using a metallising solution,

[0061] In one embodiment of the invention the substrate is a dielectric substrate and the step

iii. metal plate the substrate applying a wet-chemical plating method; comprises:

iiia. contacting the substrate with a noble metal colloid or a noble metal ion containing solution;

iiib. contacting the substrate with an electroless metal plating solution; and

iiic. contacting the substrate with an electrolytic metal plating solution.

[0062] In one embodiment of the invention at least one of the following additional method steps are performed in the overall process step iii.

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iii1. Dipping the objects or the substrates in a pre-dipping solution;

iiia1. Rinsing the objects or the substrates in a rinsing solution;

10 iiia2. Treating the objects or the substrates in an accelerating solution or in a reducing agent solution;

iiib1. Rinsing the objects or the substrates in a rinsing solution; and

iiic1. Rinsing the objects or the substrates in a rinsing solution.

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[0063] In this preferred embodiment these further method steps are carried out when the objects or the substrates are to be metallised using an electroless metallisation method which means that a first metal layer is applied on the objects or the substrates using an electroless method.

[0064] The accelerating solution preferably serves to remove components of the colloid solution according to method step iiia., for example a protective colloid. If the colloid of the colloid solution according to method step iia. is a palladium/tin colloid, a solution of an acid is preferably used as an accelerating solution, for example sulfuric acid, hydrochloric acid, citric acid or also tetrafluoroboric acid, in order to remove the protective colloid (tin compounds).

[0065] The reducing agent solution is used if a solution of a noble metal ion is used in method step (ii)a., for example a hydrochloric acid solution of palladium chloride or an acid solution of a silver salt. The reducing agent solution in this case is also a hydrochloric acid solution and, for example, contains tin(II) chloride, or it contains another reducing agent such as NaH_2PO_2 or a borane or boron hydride, such as an alkali or earth alkali borane or dimethylaminoborane.

[0066] On the other hand, a method is preferred in which the objects or the substrates are not metallised electrolessly but are to be directly metallised using an electrolytic metallisation process (without electroless metallisation).

[0067] In this embodiment of the invention the substrate is a dielectric substrate and the step

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iii. metal plate the substrate applying a wet-chemical plating method; comprises:

iiia. contacting the substrate with a noble metal colloid;

35 iiib. contacting the substrate with a conversion solution so that a sufficiently electrically conductive layer is formed on the surface of the substrate for direct electrolytic metallisation; and

iiic. contacting the substrate with an electrolytic metal plating solution.

40 **[0068]** The method steps iiid., iiie. and iiif. are performed in the sequence given, but not necessarily immediately one after the other. For example, a plurality of rinsing steps can be performed after said method steps. In this embodiment the method steps iid. and iie. act as an activation step.

[0069] The conversion solution preferably serves to create a sufficiently electrically conductive layer on the surface of the objects or the substrates in order to subsequently allow direct electrolytic metallisation, without preceding electroless metallisation. If the colloid of the colloid solution according to method step iid. is a palladium/tin colloid then an alkaline solution containing copper ions complexed with a complexing agent is preferably used as a conversion solution. For example the conversion solution can contain an organic complexing agent such as tartaric acid or ethylenediamine-tetraacetic acid and/or one of its salts, such as a copper salt, such as copper sulfate:

[0070] The conversion solution can comprise:

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(i) a Cu(II), Ag, Au or Ni soluble metal salt or mixtures thereof,

(ii) 0.05 to 5 mol/l of a group IA metal hydroxide and

55 (iii) a complexing agent for an ion of the metal of said metal salt

[0071] The treatment liquids described below are preferably aqueous.

[0072] In a preferred embodiment of the invention the solution of the colloid of the noble metal of Group VIIIB or IB of

the Periodic Table of the Elements used in the activation step is an activator solution containing a palladium/tin colloid. This colloid solution preferably contains palladium chloride, tin(II) chloride and hydrochloric acid or sulfuric acid. The concentration of the palladium chloride is preferably 5 - 200 mg/l, particularly preferred 20 - 100 mg/l and most preferred 30 - 60 mg/l, based on Pd^{2+}. The concentration of the tin(II) chloride is preferably 0.5 - 20 g/l, particularly preferred 1 - 10 g/l and most preferred 2 - 6 g/l, based on Sn^{2+}. The concentration of the hydrochloric acid is preferably 100-300 ml/l (37% by weight of HCl). Furthermore, a palladium/tin colloid solution also preferably contains tin(IV) ions which are generated through oxidation of the tin(II) ions. The temperature of the colloid solution is preferably 20 - 50°C and particularly preferred 30 - 40°C. The treatment time is preferably 0.5 - 10 min, particularly preferred 2 - 5 min and most preferred 3.5 - 4.5 min.

[0073] As an alternative the colloid solution can also contain another metal of Group VIIIB or IB of the Periodic Table of the Elements, for example platinum, iridium, rhodium, gold or silver or a mixture of these metals. It is basically possible for the colloid not to be stabilised with tin ions as a protective colloid but rather another protective colloid being used instead, for example an organic protective colloid like polyvinyl alcohol.

[0074] If a solution of a noble metal ion is used instead of a colloid solution in the activation step, preferably a solution is used which contains an acid, in particular hydrochloric acid, and a noble metal salt. The noble metal salt can, for example, be a palladium salt, preferably palladium chloride, palladium sulfate or palladium acetate, or a silver salt, for example silver acetate. As an alternative a noble metal complex can also be used, for example a palladium complex salt such as a salt of a palladium-amino complex. The noble metal compound is present, for example, in a concentration of 20 mg/l to 200 mg/l, based on the noble metal, for example based on Pd^{2+}. The solution of the noble metal compound can be used at 25°C or at a temperature from 15°C to 70°C.

[0075] Before bringing the objects or the substrates in contact with the colloid solution, the objects or the substrates are preferably first brought into contact with a pre-dipping solution which has the same composition as the colloid solution but without the metal of the colloid and its protective colloid, which means that this solution, in the case of a palladium/tin colloid solution, just contains hydrochloric acid if the colloid solution also contains hydrochloric acid. The objects or the substrates are brought directly into contact with the colloid solution after treatment in the pre-dipping solution, without rinsing off the objects or the substrates.

[0076] After treating the objects or the substrates with the colloid solution these are typically rinsed and then brought into contact with the accelerating solution in order to remove the protective colloid from the surface of the objects or the substrates.

[0077] If the objects or the substrates are treated with a solution of a noble metal ion instead of a colloid solution they will be subjected to a reduction treatment after first being rinsed. The reducing agent solution used for these cases typically contains hydrochloric acid and tin(II) chloride. If the solution of the noble metal compound is a hydrochloric acid solution of palladium chloride. It is, however, preferable to use an aqueous solution of NaH_2PO_2. Moreover, if the solution of the noble metal compound is a neutral or alkaline solution of a complex stabilized Pd sulphate or chloride, it is preferable to use an aqueous solution of DMAB (dimethyl aminoborane) or sodium borohydride in the reduction treatment.

[0078] For electroless metallisation, the objects or the substrates can first be rinsed after the acceleration or treatment with reducing agent solution and then electrolessly plated with nickel, for example. A conventional nickel bath will serve to do this which, for example, contains a number of substances including nickel sulfate, a hypophosphite, for example sodium hypophosphite, as a reducing agent, and organic complexing agents and pH adjusting agents (for example a buffer).

[0079] As an alternative, an electroless copper bath can be used which typically contains a copper salt, for example copper sulfate or copper hypophosphite, and also a reducing agent such as formaldehyde or a hypophosphite salt, for example an alkali or ammonium salt, or hypophosphorous acid, and also one or more complexing agents such as tartaric acid, as well as a pH adjusting agent such as sodium hydroxide.

[0080] Any metal depositing baths can be used for the subsequent electrolytic metallisation, for example for depositing nickel, copper, silver, gold, tin, zinc, iron, lead or their alloys. This type of depositing bath is well known to the person skilled in the art. A Watts nickel bath is normally used as a bright nickel bath which contains nickel sulfate, nickel chloride and boric acid as well as saccharine as an additive. As a bright copper bath a composition is used which, for example, contains copper sulfate, sulfuric acid, sodium chloride as well as organic sulfur compounds, in which the sulfur is present in a low oxidation stage, for example as an organic sulfide or disulfide, as additives.

[0081] If a direct electroplating process is used, that is, a first metal layer is not deposited electrolessly but rather after treatment of the objects or the substrates with the conversion solution and deposited electrolytically after the optional subsequent rinsing treatment, then an electrolytic metallisation bath is used, for example a nickel strike bath, which is preferably composed on the basis of a Watts nickel bath. These types of baths for example contain nickel sulfate, nickel chloride and boric acid and saccharine as an additive.

[0082] Treatment of the objects or the substrates according to the method according to the invention is preferably performed in a conventional dipping process in which the objects or the substrates are dipped subsequently in solutions in containers in which the respective treatment takes place. In this case the objects or the substrates can either be

fastened to racks or filled into drums and dipped in the solutions. Fastening to racks is preferred because a more directed transmission of the ultrasound energy to the objects or the substrates is possible via the racks. Alternatively, the objects or the substrates can be treated in so-called conveyorized processing plants in which they lay, for example, on racks and are continuously transported in a horizontal direction through the plant and treated with ultrasound, as required.

[0083] In another embodiment of the present invention direct metallization can be obtained by employing a conductive polymer to the surface of a dielectric substrate as for example described in US 2004/0112755 A1, US 5,447,824, and WO 89/08375 A.

[0084] EP 0 457 180 A2 discloses a method for metallizing dielectric substrates, this method comprising first forming a manganese dioxide layer on the substrate and then treating the surfaces with an acidic solution containing pyrrole and methane sulfonic acid. Instead of pyrrole the solution may also contain thiophene. Due to this treatment an electrically conducting polymer layer is formed. This electrically conducting layer may finally be electrolytically metallized. Alternatively, thiophene and aniline instead of pyrrole can be applied. Such method is suitable to be used as an activation step and subsequently to metallize non conductive substrates according to the present invention.

[0085] In this embodiment of the invention the substrate is a dielectric and the following further method steps are performed for metallization of the substrate in step iii.:

iiic. bringing the substrate into contact with a water-soluble polymer;

iiid. treating the substrate with a permanganate solution;

iiie. treating the substrate with an acidic aqueous solution or an acidic microemulsion of aqueous base containing at least one thiophene compound and at least one alkane sulfonic acid selected from the group comprising methane sulfonic acid, ethane sulfonic acid and ethane disulfonic acid;
and the step

iv. metal plate the substrate applying a wet-chemical plating method; comprises:

ivb. contacting the substrate with an electrolytic metal plating solution.

[0086] The water-soluble polymer used in step ic. preferably is selected from the group consisting of polyvinyl amine, polyethylene imine, polyvinyl imidazole, alkylamine ethylene oxide copolymers, polyethylene glycol, polypropylene glycol, copolymers of ethylene glycol and polypropylene glycol, polyvinyl alcohol, polyacrylates, polyacrylamide, polyvinylpyrrolidone and mixtures thereof. The concentration of the water-soluble polymer ranges from 20 mg/l to 10 g/l.

[0087] The solution of a water-soluble polymer may further contain a water-soluble organic solvent selected from the group consisting of ethanol, propanol, ethylene glycol, diethyleneglycol, glycerine, dioxin, butyrolacton, N-methyl pyrrolidone, dimethyl formamide, dimethylacetamide, half ethers and half esters of ethylene glycol. The water-soluble organic solvent may be utilized either in pure form or diluted with water. The concentration of the water-soluble organic solvent ranges from 10 ml/l to 200 ml/l. The solution of a water-soluble polymer is held at a temperature in the range of 25 °C to 85 °C and the dielectric substrate is immersed in this solution for 15 s to 15 min during step ic.

[0088] Next, the dielectric substrate is treated with a permanganate solution in step id. The source of permanganate ions can be any water-soluble permanganate compound. Preferably the source of permanganate ions is selected from sodium permanganate and potassium permanganate. The concentration of permanganate ions ranges from 0.1 mol/l to 1.5 mol/l. The permanganate solution can be either acidic or alkaline. Preferably, the permanganate solution has a pH value in the range of 2.5 to 7. By means of step id. a layer of MnO_2 is formed on the side walls of a blind micro via (BMV).

[0089] The substrate is then contacted in step ie. with a solution comprising preferably a thiophene compound and an alkane sulfonic acid.

[0090] The thiophene compound is preferably selected from 3-heterosubstituted thiophenes and 3,4-heterosubstituted thiophenes. Most preferably, the thiophene compound is selected from the group consisting of 3,4-ethylene dioxythiophene, 3-methoxy thiophene, 3-methyl-4-methoxy thiophene and derivatives thereof. The concentration of the thiophene compound ranges from 0.001 mol/l to 1 mol/l, more preferably from 0.005 mol/l to 0.05 mol/l.

[0091] The alkane sulfonic acid is selected from the group comprising methane sulfonic acid, ethane sulfonic acid, methane disulfonic acid, ethane disulfonic acid and mixtures thereof. The concentration of the alkane sulfonic acid is set by adjusting the desired pH value of the solution utilized in step ie. Preferably the pH value of said solution is set in the range of 0 to 3, more preferably in the range of 1.5 to 2.1.

[0092] For the purposes of the present invention plating of copper as metal is particularly preferred. In printed circuit board applications the total thickness of the deposited a copper layer or layers generally ranges between 1 and 50 μm, more preferably between 4 and 30 μm.

Examples

[0093] The following experiments are meant to illustrate the benefits of the present invention without limiting its scope.

[0094] In the experiments the different silanes employed are listed and identified in Table 1. The following organic solvents were used to dissolve the silanes: isopropanol (bp 82 °C: denoted in the following as IPA), and 2-isopropoxyethanol (bp 142 °C, in the following denoted as IPPE).

[0095] Sample Nos. **P1, P6** through **P9,** and **P11** through **P 20** were first treated with a silane composition and then treated in an aqueous solution containing MnO_4-ions. For sample No. **P2** the process sequence was changed: treatment in an aqueous solution containing MnO_4-ions was first and then followed by treatment in the silane composition (comparative example). For sample No. **P3** the treatment in an aqueous solution containing MnO_4-ions was omitted and only the silane composition was applied (also comparative example). Sample No. **P4** was processed in an aqueous solution containing MnO_4-ions only, without any silane treatment (comparative example). Samples Nos. **P5** and **P10** were first treated with the solvent matrix without the silane compound and then treated in an aqueous solution containing MnO_4-ions (comparative examples). The permanganate treatment step was always followed by a reducer step to remove the manganese(IV)oxide. The corresponding process conditions are provided in Table 1.

[0096] Compositions are provided in Table 1. Treatment time was 1 min at ambient temperature.

[0097] The base material used was an epoxy resin ABF GX92 from Ajinomoto Co.; Inc. For the experiments, samples (7.5 x 15 cm) were cut out of panels laminated and pre-cured for 30 minutes at a temperature of 100°C followed by 30 minutes at a temperature of 180 °C.

[0098] All solutions were freshly made up before spraying. Silane content is given in weight percent and was 3 wt.% for all experiments performed.

[0099] Silane application: The solution (excluding example **P4)** was sprayed onto the substrate using the ExactaCoat spray device by Sonotek. For examples **P5** and **P10** the solvent does not contain a silane and was applied the same way. Following parameters were set for all investigations:

Flow rate:	1.4 ml/min. (6 ml/min.)
Nozzle Distance:	4 cm
Nozzle Speed:	40 mm/s
Overlap:	14.2 mm
Nitrogen flow:	0.8 - 1.0 mPa

One spray cycle

[0100] Afterwards the panels were held for 10 minutes before baking them at 105°C for 5 min. Panels were allowed to cool down to room temperature and passed to the permanganate etchant (excluding sample **P3).**

[0101] Sample **P2** was first processed through the permanganate etchant and reduction solution and sprayed afterwards. No second MnO_4-etch step was included. Additional comparative examples P21 and P22 have been carried out in solutions containing sulphuric acid and hydrogen peroxide.

[0102] Example **P21** was performed according to the foregoing process sequence wherein the solution comprising an oxidizing agent contained in a volume ratio of 3 to 1 concentrated sulphuric acid and 30 wt.% hydrogen peroxide. Treatment was performed at a temperature of 60°C for 10 seconds. Despite obtaining a rather high roughness value subsequent metal plating resulted in a very poor adhesion of the metal layer to the surface substrate, thus rendering this treatment method unsuitable to produce an adherent metal layer which is the purpose of the present invention. Higher treatment time and / or higher temperatures resulted in complete removal of the resin layer and no adhesion of the subsequently plated metal layer.Example **P22** was performed according to the foregoing process sequence wherein the solution comprising an oxidizing agent contained 20 mL/L concentrated sulphuric acid and 20 mL/L 30 wt.% hydrogen peroxide. Treatment was performed at a temperature of 25°C for 5 minutes.The surface treated showed a low roughness and very poor adhesion of the subsequently plated metal layer, rendering this solution to produce an adherent metal layer which is the purpose of the present invention.

Table 1: Sample names and process conditions.

Exp. No.	Silane (3% wt.)	Solvent	Treatment	Peel Strength N/cm	Average Roughness (Ra) nm
			1. Silane;		

(continued)

Exp. No.	Silane (3% wt.)	Solvent	Treatment	Peel Strength N/cm	Average Roughness (Ra) nm
P1	3-Aminopropyltri-ethoxysilane	IPA	2. MnO4 + Reducer	5.53	102
P2*	Ami-nopropyltrieth-oxysilane	IPA	1. MnO4 + Reducer; 2. Silane	0.86	96
P3*	Ami-nopropyltriethoxysilane	IPA	only Silane	0.08	80
P4*	No	No	only Mn04 + Reducer	0.78	96
P5*	No	IPA	1. only Solvent Treatment; 2. MnO4 + Reducer	2.00	95
P6	3-Glycidoxy-propyl-trimethoxysilane	IPA	1. Silane; 2. Mn04 + Reducer	7.33	82
P7	Vinyl tris(2-methoxyethoxy)silane	IPA	1. Silane; 2. MnO4 + Reducer	4.4	90
P8	N-Styryl-methyl-2-aminoethylamino)-propyltri-methoxysilane	IPA	1. Silane; 2. Mn04 + Reducer	7.0	109
P9	1-[2-(Trimethoxy-silyl)ethyl]cyclohe xane-3, 4-epoxide	IPA	1. Silane; 2. MnO4 + Reducer	4.6	76
P10*	No	IPPE	1. only Solvent Treatment 2. MnO4 + Reducer	3.0	77
P11	3-Aminopropyltriethoxysilane	IPPE	1. Silane; 2. Mn04 + Reducer	6.9	94
P12	3-Chloro propyltri-methoxy silane	IPPE	1. Silane; 2. MnO4 + Reducer	5.30	95
P13	3-Glycidoxy propyltri-methoxy silane	IPPE	1. Silane; 2. Mn04 + Reducer	7.0	96
P14	Vinyl tris (2-methoxyethoxy)silane	IPPE	1. Silane; 2. MnO4 + Reducer	6.9	98
P15	Ethyltriacetoxy silane	IPPE	1. Silane; 2. MnO4 + Reducer	5.5	93

(continued)

Exp. No.	Silane (3% wt.)	Solvent	Treatment	Peel Strength N/cm	Average Roughness (Ra) nm
P16	3-(Trimethoxy silyl)propyl methacrylate	IPPE	1. Silane; 2. MnO4 + Reducer	5.4	87
P17	N-Styrylmethyl-2-aminoethylamino)propyl trimethoxysilane	IPPE	1. Silane; 2. MnO4 + Reducer	7.0	113
P18	Phenyltrimethoxysilane	IPPE	1. Silane; 2. MnO4 + Reducer	4.7	76
P19	1-[2-(Trimethoxy silyl)ethyl]cyclohe xane-3,4 epoxide	IPPE	1. Silane; 2. MnO4 + Reducer	5.2	88
P20	1-[3-(Trimethoxy silyl)propyl]urea	IPPE	1. Silane; 2. MnO4 + Reducer	8.0	109
P21*	3-Aminopropyltriethoxysilane	IPA	1. Silane; 2. H2SO4 / H2O2	2.1	130
P22*	3-Aminopropyltriethoxysilane	IPA	1. Silane; 2. H2SO4 / H2O2	1.3	67

*** comparative Examples**
MnO4 denotes MnO_4^{--} ions

[0103] Figure 2 shows a surface after permanganate treatment of GX92 substrate material according to example P20. Measurement was performed on a Zeiss Gemini SEM, voltage 5 kV, magnification: 5000 x.

[0104] The roughness Ra measured was 109 nm measured by an Olympus LEXT 3000 confocal laser microscope.

[0105] Figure 3 shows an SEM image of a surface after permanganate treatment without prior application of a silane of GX92 substrate material. This corresponds to a method known in the art involving a waterbased Sweller followed by Permanganate-Etching. Permanganate concentration was 60 g/l, NaOH conc. 45 g/l, treatment time 20 minutes, and temperature 80°C. The roughness Ra measured by above mentioned confocal laser microscope was 200 nm. Such roughness can be too high for manufacture of fine line circuitry.

[0106] Thereafter, the samples were metal plated according to the process parameters provided in Table 2. Table 2 comprises of the process sequence applied to finally deposit 0.8 μm of electroless copper and 30 μm electrolytically deposited copper on GX92 substrate material.

Table 2: Parameters used for subsequent metal plating

Step No.	Name	T [°C]	t [min]
1	Permanganate Etch (45 g/l MnO_4^-, 45 g/l NaOH)	75	15
	DI Rinse		
2	MnO_4 Reduction sol.	50	4
	DI Rinse		
3	Cleaner	60	4
	DI Rinse		
4	NaPS/H_2SO_4	35	1
	DI Rinse		

(continued)

Step No.	Name	T [°C]	t [min]
5	Pre-Dip	25	1
6	Neoganth Activator	40	4
	DI Rinse		
7	Neoganth Reducer	30	3
	DI Rinse		
8	Electroless Cu	34	15
	DI Rinse, air dry		
9	Electroless Cu Annealing	150	30
10	H_2SO_4 Pre-Dip	25	1
11	Acid Cu	25	90
	Current Density: 2 A/dm^2 Copper Thickness: 30 μm		
	DI Rinse, air dry		
12	Acid Cu Annealing	180	60

[0107] Peel strength measurements of the plated metal layer to the substrate were performed by routing the samples in stripes of 1 cm width and 3 cm length after final annealing. Peel strength measurements were performed with an Erichsen Wuppertal 708 strain gauge using a Chatillon LTCM-6 pulling mechanism The adhesion values for all samples are depicted in Table 1, 5th ("Peel") column.

[0108] Field Emission Scanning Electron Microscopy (FE-SEM) was performed using a LEO 1530 with 5 kV accelerating voltage and a silicon drift detector (Xmas 80, Oxford). Images were recorded with a magnification of 5000. Dielectric surface was measured after etching the plated copper using sulphuric acid/hydrogen peroxide (50 ml/L conc. H_2SO_4, 53 ml/L H_2O_2 in water at 40°C). Samples were sputtered with Iridium before measurement.

[0109] For commercial processes, for example flip-chip ball-grid-arrays, typically adhesion values of greater than 4 - 5 N/cm are required. This depends on the type of application.

[0110] Average roughness values (Ra) were measured on an Olympus LEXT 3000 confocal laser microscope. Roughness values were gathered over a surface area of 120 μm by 120 μm. The average roughness values (Ra) for all samples are depicted in Table 1, 6th column (Average Roughness Ra).

[0111] Sufficient adhesion between the plated metal layer and the substrate could only be obtained by treatment of the samples with a process according to the present invention, i.e. a silane-based treatment of the substrate surface first which is followed by the permanganate treatment step. All other combinations of the process sequence as shown in Table 1 result in very low adhesion of the plated metal layer which is not acceptable for commercial applications.

[0112] The lowest adhesion values were found for the sample P3 coated with silanes only (without any permanganate treatment) and then subsequently metallized. A slightly increase of initial adhesion was seen when the permanganate treatment was applied before the metal plating steps of the substrate (Sample No. P4). This increase was caused by an additional roughening of the surface due to the permanganate step. However, all samples which were not processed through permanganate after the silane coating showed blister on the surface after the final copper annealing. Therefore a permanganate rinse is preferable after the silane coating.

[0113] By changing the first two main steps in the process sequence it was demonstrated that only the correct sequence (first silane treatment followed by permanganate cleaner) resulted in significant adhesion increase (up to 5.5 N/cm). All other combinations (silane only, MnO_4 only as well as first MnO_4 then silane treatment) gave very low adhesion < 1.0 N/cm.

[0114] The low roughness values of the treated samples render the process suitable for manufacture of circuit traces which are smaller than 10 um width. For such structures surface roughness values over 150 nm were hitherto required to achieve sufficient adhesion between the substrate and the plated metal layer. However, average roughness values higher than 150 nm may be too high for circuit traces smaller than 10 um in width.

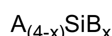
Claims

1. A method for treating a surface of a dielectric substrate to prepare said surface for subsequent wet chemical metal plating, such method comprising in this order the steps of

   (i) treating said surface with a solution comprising at least one organosilane compound;
   (ii) treating said surface with a solution comprising an oxidizing agent selected from aqueous acidic or alkaline solutions of a permanganate salt.

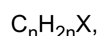
2. Method according to claim 1 wherein the concentration of permanganate salt ranges from 20 - 100 g/l.

3. Method according to claim 1 wherein the organosilane compound is selected from the group represented by the formula



$$A_{(4-x)}SiB_x$$

wherein
each A is independently a hydrolyzable group,
x is 1 to 3, and
each B is independently selected from the group consisting of C_1-C_{20} alkyl, aryl, amino aryl and a functional group represented by the formula



$$C_nH_{2n}X,$$

wherein
n is from 0 to 15, preferably 0 to 10 even more preferably 1 to 8, most preferably 1, 2, 3, 4 and
X is selected from the group consisting of amino, amido, hydroxy, alkoxy, halo, mercapto, carboxy, carboxy ester, carboxamide, thiocarboxamide, acyl, vinyl, allyl, styryl, epoxy, epoxycyclohexyl, glycidoxy, isocyanato, thiocyanato, thioisocyanato, ureido, thioureido, guanidino, thioglycidoxy, acryloxy, methacryloxy groups; or X is a residue of a carboxy ester; or X is $Si(OR)_3$, and wherein R is a C_1-C_5 alkyl group.

4. Method according to claim 3 wherein the hydrolyzable group A is selected from the group consisting of -OH, $-OR^1$ and wherein R^1 is C_1-C_5 alkyl, - $(CH_2)_yOR^2$ and wherein y is 1, 2 or 3 and R^2 is H or C_1-C_5 alkyl, $-OCOR^3$ and and wherein R^3 is H or C_1-C_5 alkyl.

5. Method according to claim 4, wherein R^1, R^2 and R^3 are independently selected from methyl, ethyl, propyl and isopropyl.

6. Method according to to any of the foregoing claims wherein the organosilane compound is selected from the group consisting of vinylsilanes, aminoalkylsilanes, ureidoalkylsilanes, methacryloxy silanes and epoxyalkylsilanes.

7. Method according to to any of the foregoing claims wherein the organosilane is applied in a concentration of between 0.5 wt.% and 20 wt.%.

8. Method according to to any of the foregoing claims wherein the organosilane is dissolved in a polar organic solvent organic solvent having boiling point in the range of 60 to 250 °C.

9. Method according to to any of the foregoing claims wherein the organosilane is dissolved in a polar organic solvent selected from diethyleneglycol, 2-isopropoxyethanol (IPPE), di(propyleneglycol)methyletheracetate (DPGMEA), and 2-ethyl-1-hexanol.

10. Method according to any of the foregoing claims wherein the oxidizing agent according to step 1 ii) is an alkaline aqueous solution of permanganate ions.

11. Method according to any of the foregoing claims comprising

    (i) treating said surface with a solution comprising at least one organosilane compound for a period of time of between 10 s and 10 min. at a temperature of between 15 and 50 °C

(ii) treating said surface with a solution comprising an oxidizing agent selected from an alkaline aqueous solution of permanganate ions in a concentration of 20 - 100 g/l for a period of time of between 1 and 30 min. at a temperature of between 20 and 95 °C to obtain a roughened surface having an average surface roughness Ra of less than 150 nm.

12. Method according to any of the foregoing claims further comprising

(iii) metallizing the substrate after step (ii) with a wet chemical plating method.

13. Method according to claim 12 wherein metallizing is a copper metallizing.

14. Method according to claims 12 and 13 wherein

(iii) metallizing the substrate after step (ii) with a wet chemical plating method comprises the following steps to render the surface conductive
(iii a) contacting the substrate with an activator solution, that contains colloidal or ionic catalysing metal, such as a noble metal, preferably palladium, causing the the substrate's surface to become catalytic,
and optionally, particularly if the activator contains ionic catalysing metal,
(iii b) contacting the substrate with a reducer, wherein the metal ions of an ionic activator are reduced to elemental metal,
or, if the activator contains colloidal catalysing metal,
(iii c) contacting the substrate with an accelerator, wherein the components of the colloid, for example a protective colloid, is removed from the catalysing metal.

15. Method according to any of the claims 1 to 12 wherein the dielectric substrate is a substrate comprising a bare dielectric build-up layer (1) having on at least a portion of the back side a contact area (2) and a second dielectric layer (3) attached to the back side of the build-up layer (1), having at least one opening (4) in the build-up layer (1) which extends through the substrate to the contact area (2),

(i) treating said surface with a solution comprising at least one organosilane compound as defined in any of the aforementioned claims,
(ii) treating said surface with a solution comprising an oxidizing agent as defined in any of the aforementioned claims,
(iii) depositing a conductive seed layer (6) onto the top surface (5a) of the dielectric build-up layer (1) and the dielectric side walls (5b) of the at least one opening (4), and
(iv) selectively depositing a copper layer (8) into openings of a patterned resist layer (7) by electroplating.

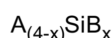
Patentansprüche

1. Verfahren zum Behandeln einer Oberfläche eines dielektrischen Substrats zur Vorbereitung der Oberfläche für die anschließende nasschemische Metallabscheidung, wobei das Verfahren folgende Schritte in der angegebenen Reihenfolge umfasst:

(i) Behandeln der Oberfläche mit einer mindestens eine Organosilanverbindung umfassenden Lösung;
(ii) Behandeln der Oberfläche mit einer ein aus wässrigen sauren oder alkalischen Lösungen eines Permanganatsalzes ausgewähltes Oxidationsmittel umfassenden Lösung.

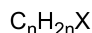
2. Verfahren nach Anspruch 1, bei dem die Permanganatsalz-Konzentration im Bereich von 20-100 g/l liegt.

3. Verfahren nach Anspruch 1, bei dem die Organosilanverbindung aus der Gruppe, die durch die Formel



$$A_{(4-x)}SiB_x$$

wiedergegeben wird, ausgewählt wird, wobei A jeweils unabhängig für eine hydrolysierbare Gruppe steht,
x für 1 bis 3 steht und
B jeweils unabhängig aus der Gruppe bestehend aus C_1-C_{20}-Alkyl, Aryl, Aminoaryl und einer funktionellen Gruppe der Formel



ausgewählt ist, wobei
n für 0 bis 15, vorzugsweise 0 bis 10, noch weiter bevorzugt 1 bis 8 und ganz besonders bevorzugt 1, 2, 3 oder 4 steht und
X aus der Gruppe bestehend aus Amino-, Amido-, Hydroxy-, Alkoxy-, Halogen-, Mercapto-, Carboxy-, Carboxyester-, Carboxamid-, Thiocarboxamid-, Acyl-, Vinyl-, Allyl-, Styryl-, Epoxy-, Epoxycyclohexyl-, Glycidoxy-, Isocyanato-, Thiocyanato-, Thioisocyanato-, Ureido-, Thioureido-, Guanidino-, Thioglycidoxy-, Acryloxy- und Methacryloxygruppen ausgewählt ist oder X für einen Rest eines Carboxyesters steht oder X für $Si(OR)_3$ steht und wobei R für eine C_1-C_5-Alkylgruppe steht.

4. Verfahren nach Anspruch 3, bei dem die hydrolysierbare Gruppe A aus der Gruppe bestehend aus -OH und -OR^1 ausgewählt ist und wobei R^1 für C_1-C_5-Alkyl oder -$(CH_2)_yOR^2$ steht und wobei y für 1, 2 oder 3 steht und R^2 für H, C_1-C_5-Alkyl oder -$OCOR^3$ steht und wobei R^3 für H oder C_1-C_5-Alkyl steht.

5. Verfahren nach Anspruch 4, bei dem R^1, R^2 und R^3 unabhängig aus Methyl, Ethyl, Propyl und Isopropyl ausgewählt sind.

6. Verfahren nach einem der vorhergehenden Ansprüche, bei dem die Organosilanverbindung aus der Gruppe bestehend aus Vinylsilanen, Aminoalkylsilanen, Ureidoalkylsilanen, Methacryloxysilanen und Epoxyalkylsilanen ausgewählt wird.

7. Verfahren nach einem der vorhergehenden Ansprüche, bei dem das Organosilan in einer Konzentration zwischen 0,5 Gew.-% und 20 Gew.-% angewendet wird.

8. Verfahren nach einem der vorhergehenden Ansprüche, bei dem das Organosilan in einem polaren organischen Lösungsmittel mit einem Siedepunkt im Bereich von 60 bis 250°C gelöst wird.

9. Verfahren nach einem der vorhergehenden Ansprüche, bei dem das Organosilan in einem aus Diethylenglykol, 2-Isopropoxyethanol (IPPE), Di(propylenglykol)methyletheracetat (DPGMEA) und 2-Ethyl-1-hexanol ausgewählten polaren organischen Lösungsmittel gelöst wird.

10. Verfahren nach einem der vorhergehenden Ansprüche, bei dem es sich bei dem Oxidationsmittel gemäß Schritt 1 ii) um eine alkalische wässrige Lösung von Permanganationen handelt.

11. Verfahren nach einem der vorhergehenden Ansprüche, umfassend:

(i) Behandeln der Oberfläche mit einer mindestens eine Organosilanverbindung umfassenden Lösung über einen Zeitraum zwischen 10 s und 10 min bei einer Temperatur zwischen 15 und 50°C;
(ii) Behandeln der Oberfläche mit einer ein aus einer alkalischen wässrigen Lösung von Permanganationen in einer Konzentration von 20 - 100 g/l ausgewähltes Oxidationsmittel umfassenden Lösung über einen Zeitraum zwischen 1 und 30 min bei einer Temperatur zwischen 20 und 95°C zum Erhalt einer aufgerauten Oberfläche mit einer durchschnittlichen Oberflächenrauheit Ra von weniger als 150 nm.

12. Verfahren nach einem der vorhergehenden Ansprüche, ferner umfassend:

(iii) Metallisieren des Substrats nach Schritt (ii) durch ein nasschemisches Metallabscheidungsverfahren.

13. Verfahren nach Anspruch 12, bei dem es sich bei der Metallisierung um eine Kupfermetallisierung handelt.

14. Verfahren nach Anspruch 12 und 13, bei dem (iii) das Metallisieren des Substrats nach Schritt

(ii) durch ein nasschemisches Metallabscheidungsverfahren die folgenden Schritte zum Leitfähigmachen der Oberfläche umfasst:
(iiia) Kontaktieren des Substrats mit einer Aktivatorlösung, die kolloidales oder ionisches katalysierendes Metall, wie ein Edelmetall,
vorzugsweise Palladium, enthält, wodurch die Substratoberfläche katalytisch wird,

und gegebenenfalls, insbesondere dann, wenn der Aktivator ionisches katalysierendes Metall enthält,
(iiib) Kontaktieren des Substrats mit einem Reduktionsmittel, wobei die Metallionen eines ionischen Aktivators zu elementarem Metall reduziert werden,
oder dann, wenn der Aktivator kolloidales katalysierendes Metall enthält,
(iiic) Kontaktieren des Substrats mit einem Beschleuniger, wobei die Komponenten des Kolloids, beispielsweise ein Schutzkolloid, von dem katalysierenden Metall entfernt werden.

15. Verfahren nach einem der Ansprüche 1 bis 12, bei dem es sich bei dem dielektrischen Substrat um ein Substrat handelt, das eine blanke dielektrische Aufbauschicht (1), die auf mindestens einem Teil der Rückseite einen Kupferbereich (2) aufweist, und eine auf der Rückseite der Aufbauschicht (1) angebrachte zweite dielektrische Schicht (3) mit mindestens einer Öffnung (4) in der Aufbauschicht (1), die sich durch das Substrat bis zum Kontaktbereich (2) erstreckt, umfasst, umfassend:

(i) Behandeln der Oberfläche mit einer mindestens eine Organosilanverbindung umfassenden Lösung gemäß einem der vorhergehenden Ansprüche,
(ii) Behandeln der Oberfläche mit einer ein Oxidationsmittel enthaltenden Lösung gemäß einem der obigen Ansprüche,
(iii) Abscheiden einer leitfähigen Keimschicht (6) auf der oberen Oberfläche (5a) der dielektrischen Aufbauschicht (1) und den dielektrischen Seitenwänden (5b) der mindestens einen Öffnung (4) und
(iv) selektives Abscheiden einer Kupferschicht (8) in Öffnungen einer strukturierten Resistschicht (7) durch Galvanisierung.

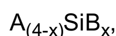
Revendications

1. Procédé de traitement d'une surface d'un substrat diélectrique pour préparer ladite surface à un dépôt chimique humide de métal, un tel procédé comprenant, dans cet ordre, les étapes consistant à

(i) traiter ladite surface avec une solution comprenant au moins un composé d'organosilane ;
(ii) traiter ladite surface avec une solution comprenant un oxydant choisi parmi les solutions aqueuses acides ou alcalines d'un sel de permanganate.

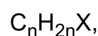
2. Procédé selon la revendication 1 dans lequel la concentration de sel de permanganate va de 20 à 100 g/l.

3. Procédé selon la revendication 1 dans lequel le composé d'organosilane est choisi dans le groupe représenté par la formule



$$A_{(4-x)}SiB_x,$$

dans laquelle
chaque A représente indépendamment un groupe hydrolysable,
x vaut 1 à 3, et
chaque B est indépendamment choisi dans le groupe constitué par un alkyle en C_1-C_{20}, un aryle, un aminoaryle et un groupe fonctionnel représenté par la formule



$$C_nH_{2n}X,$$

dans laquelle
n vaut de 0 à 15, de préférence 0 à 10, mieux encore 1 à 8, idéalement 1, 2, 3, ou 4 et
X est choisi dans le groupe constitué par les groupes amino, amido, hydroxyle, alcoxy, halogéno, mercapto, carboxyle, carboxyester, carboxamide, thiocarboxamide, acyle, vinyle, allyle, styryle, époxy, époxycyclohexyle, glycidoxy, isocyanato, thiocyanato, thioisocyanato, uréido, thiouréido, guanidino, thioglycidoxy, acryloxy, et méthacryloxy ; ou bien X est un résidu d'un carboxyester ; ou bien X représente $Si(OR)_3$ où R est un groupe alkyle en C_1-C_5.

4. Procédé selon la revendication 3 dans lequel le groupe hydrolysable A est choisi dans le groupe constitué par -OH, $-OR^1$ où R^1 est un alkyle en C_1-C_5,$-(CH_2)_yOR^2$ où y vaut 1, 2 ou 3 et R^2 représente H ou un alkyle en C_1-C_5, et $-OCOR^3$ où R^3 représente H ou un alkyle en C_1-C_5.

5. Procédé selon la revendication 4, dans lequel R^1, R^2 et R^3 sont indépendamment choisis parmi les groupes méthyle, éthyle, propyle et isopropyle.

6. Procédé selon l'une quelconque des revendications précédentes dans lequel le composé d'organosilane est choisi dans le groupe constitué par les vinylsilanes, les aminoalkylsilanes, les uréidoalkylsilanes, les méthacryloxysilanes et les époxyalkylsilanes.

7. Procédé selon l'une quelconque des revendications précédentes dans lequel l'organosilane est appliqué à une concentration comprise entre 0,5 % en poids et 20 % en poids.

8. Procédé selon l'une quelconque des revendications précédentes dans lequel l'organosilane est dissous dans un solvant organique polaire ayant un point d'ébullition dans la gamme de 60 à 250 °C.

9. Procédé selon l'une quelconque des revendications précédentes dans lequel l'organosilane est dissous dans un solvant organique polaire choisi parmi le diéthylène glycol, le 2-isopropoxyéthanol (IPPE), l'acétate d'éther méthylique de di(propylène glycol) (DPGMEA), et le 2-éthyl-1-hexanol.

10. Procédé selon l'une quelconque des revendications précédentes dans lequel l'oxydant selon l'étape 1 ii) est une solution aqueuse alcaline d'ions permanganate.

11. Procédé selon l'une quelconque des revendications précédentes comprenant

(i) le traitement de ladite surface avec une solution comprenant au moins un composé d'organosilane pendant un laps de temps compris entre 10 s et 10 min à une température comprise entre 15 et 50 °C,
(ii) le traitement de ladite surface avec une solution comprenant un oxydant choisi parmi les solutions aqueuses alcalines d'ions permanganate à une concentration de 20-100 g/l pendant un laps de temps compris entre 1 et 30 min à une température comprise entre 20 et 95 °C pour obtenir une surface rugosifiée ayant une rugosité de surface moyenne Ra de moins de 150 nm.

12. Procédé selon l'une quelconque des revendications précédentes comprenant en outre

(iii) la métallisation du substrat après l'étape (ii) avec un procédé de dépôt chimique humide.

13. Procédé selon la revendication 12 dans lequel la métallisation est une métallisation au cuivre.

14. Procédé selon les revendications 12 et 13 dans lequel

(iii) la métallisation du substrat après l'étape (ii) avec un procédé de dépôt chimique humide comprend les étapes suivantes pour rendre la surface conductrice :

(iii a) mettre le substrat en contact avec une solution d'activateur, qui contient un métal catalysant colloïdal ou ionique, tel qu'un métal noble, de préférence du palladium, pour amener la surface du substrat à devenir catalytique,
et éventuellement, en particulier si l'activateur contient un métal catalysant ionique,
(iii b) mettre le substrat en contact avec un réducteur, les ions métalliques d'un activateur ionique étant réduit en métal élémentaire,
ou, si l'activateur contient un métal catalysant colloïdal,
(iii c) mettre le substrat en contact avec un accélérateur, les composants du colloïde, par exemple un colloïde protecteur, étant retirés du métal catalysant.

15. Procédé selon l'une quelconque des revendications 1 à 12 dans lequel le substrat diélectrique est un substrat comprenant une couche d'accumulation diélectrique nue (1) ayant sur au moins une partie de la face arrière une zone de contact (2) et une deuxième couche diélectrique (3) attachée à la face arrière de la couche d'accumulation (1), ayant au moins une ouverture (4) dans la couche d'accumulation (1) qui s'étend à travers le substrat jusqu'à la zone de contact (2), comprenant

(i) le traitement de ladite surface avec une solution comprenant au moins un composé d'organosilane tel que défini dans l'une quelconque des revendications précédentes,

(ii) le traitement de ladite surface avec une solution comprenant un oxydant tel que défini dans l'une quelconque des revendications précédentes,
(iii) le dépôt d'une couche de germination conductrice (6) sur la surface supérieure (5a) de la couche d'accumulation diélectrique (1) et les parois latérales diélectriques (5b) de l'au moins une ouverture (4), et
(iv) le dépôt sélectif d'une couche de cuivre (8) dans les ouvertures d'une couche de réserve structurée (7) par dépôt électrolytique.

Fig. 1

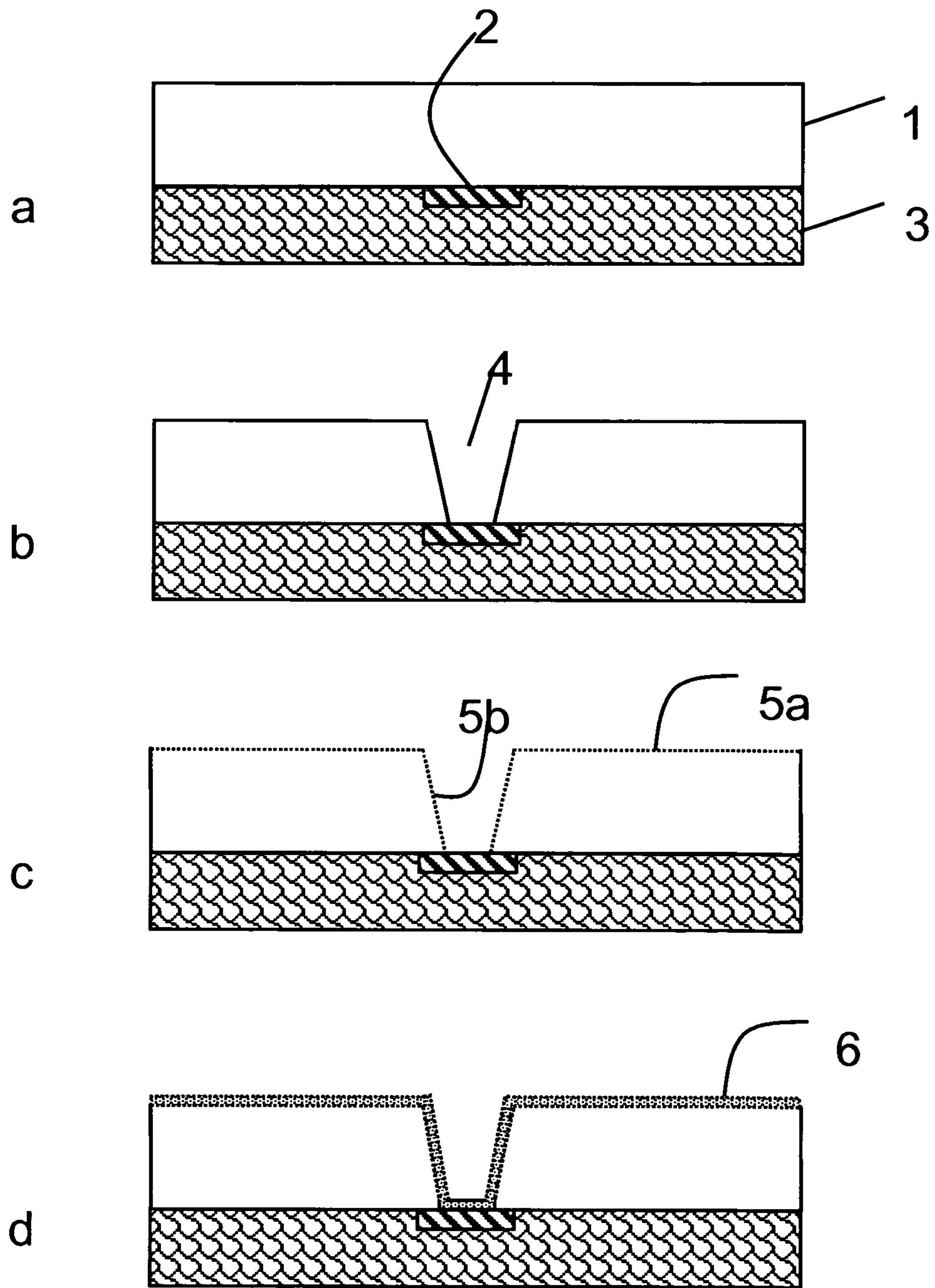


Fig. 1 (cont.)

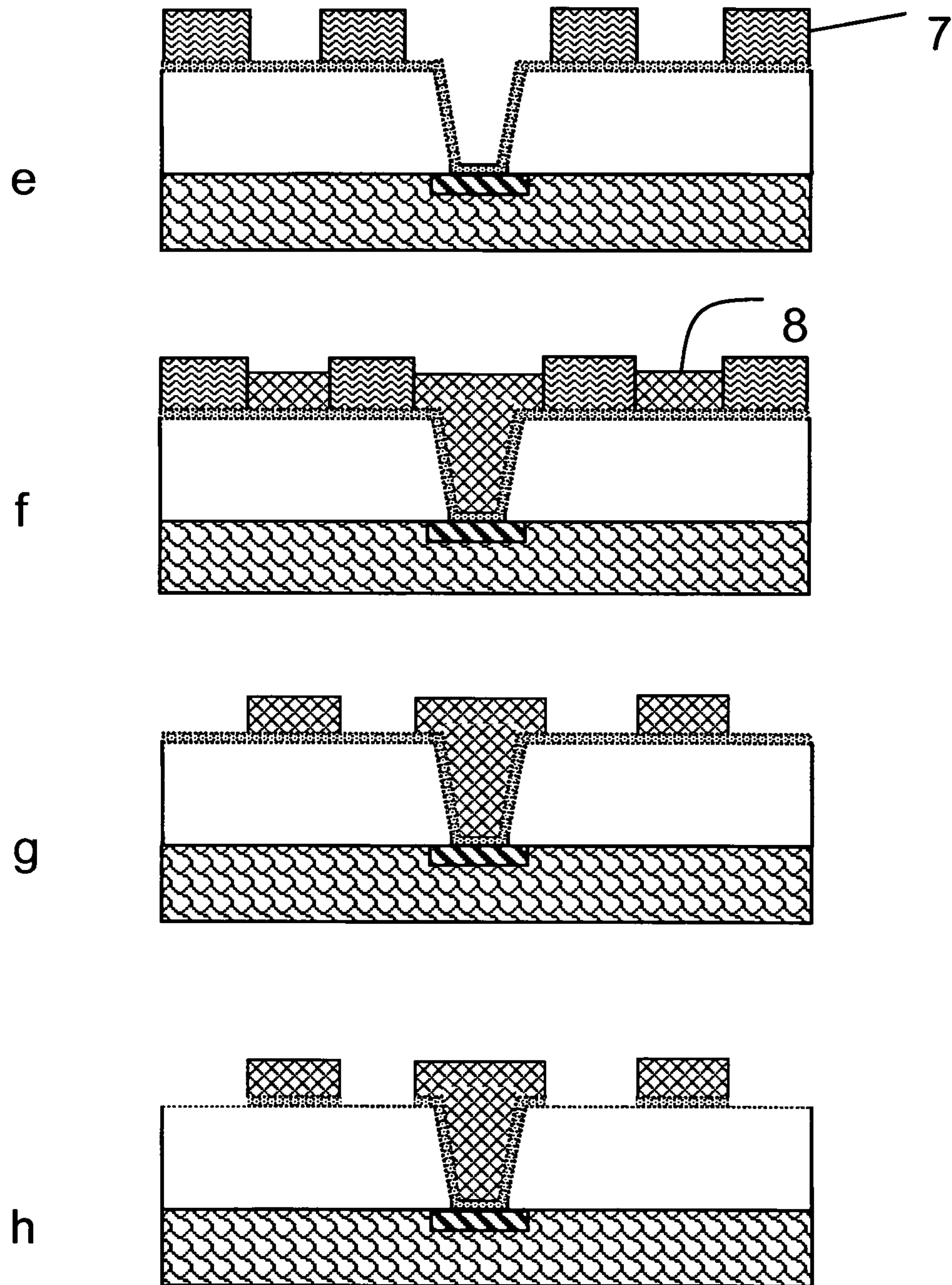


Fig. 2

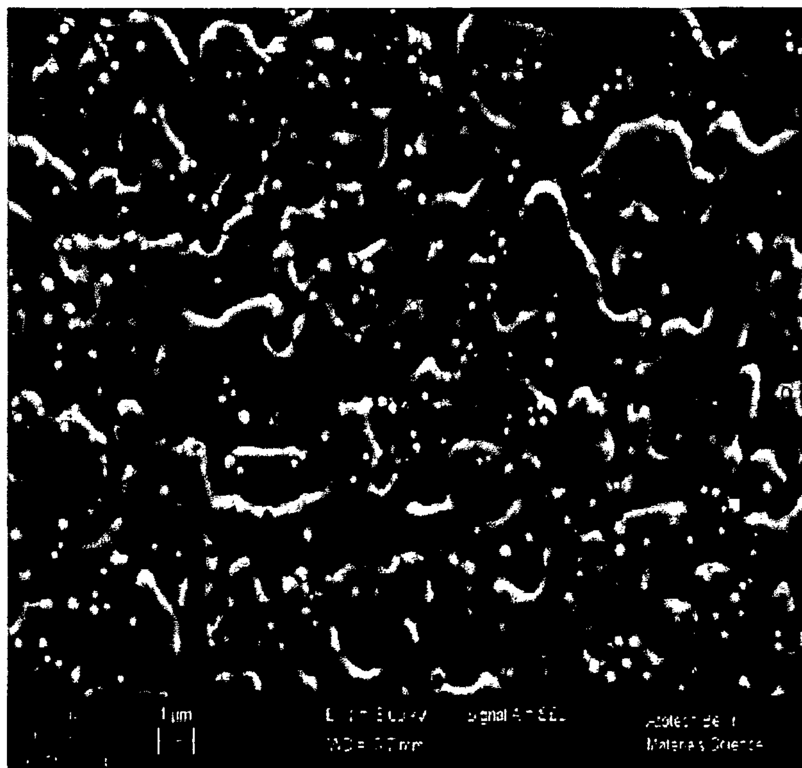
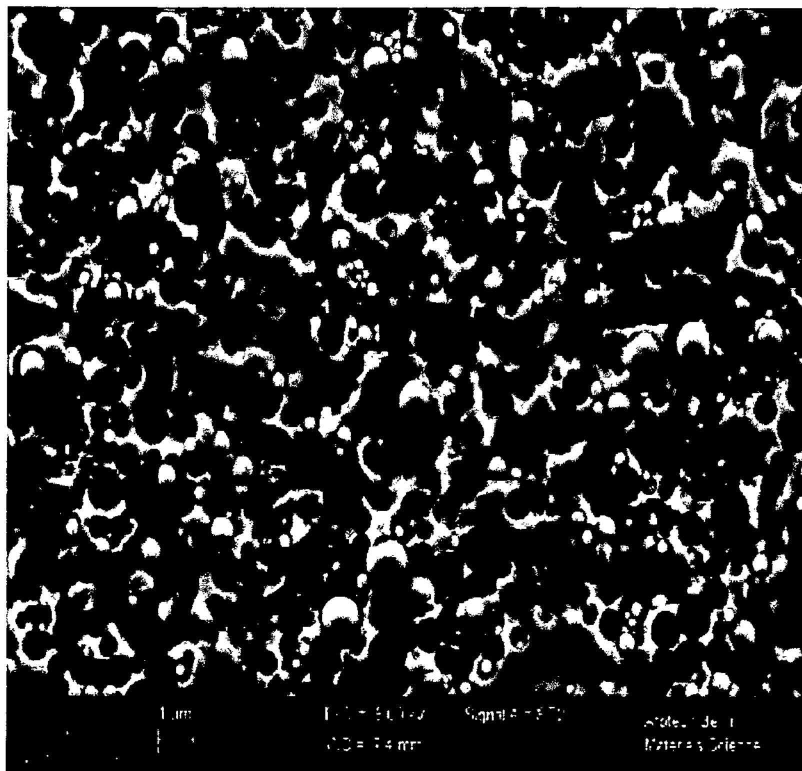


Fig. 3



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