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(54) Title: METHOD OF FORMING COPPER OXIDE ON A COPPER SURFACE

(57) Abstract: A method of forming copper oxide on a copper surface, the method comprising the steps a) providing a substrate comprising the copper surface, b) optionally pre-cleaning the copper surface, c) contacting the copper surface with an alkaline aqueous oxidizing solution comprising one or more than one oxidizing compound selected from the group consisting of - an aromatic sulfonic acid compound, salts thereof, - an aromatic sulfonic acid ester compound, salts thereof, - an aromatic nitro compound, and salts thereof, such that said copper oxide is formed on the copper surface.



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METHOD OF FORMING COPPER OXIDE ON A COPPER SURFACE

FIELD OF THE INVENTION

The present invention relates to a method of forming copper oxide on a copper surface and a use of specific oxidizing compounds in an alkaline aqueous oxidizing solution to form uniform copper oxide on a copper surface.

BACKGROUND OF THE INVENTION

In the production of electronic articles which comprise a copper surface, passivation is often desired. Passivation may be done for reasons of protection for example by means of a layer of copper oxide. The copper oxide is typically later partially or fully removed for further process steps in the production of the electronic article.

Strong aqueous alkaline solutions, which primarily serve as cleaning solutions, often also lead to the formation of passivating copper oxide. However, it has been shown that the oxidation process is often very slow, leads to relatively thin and/or inhomogeneous copper oxide.

Moreover, using such an aqueous alkaline solution, solubilization of carbon dioxide from ambient air typically leads to a decrease in pH, thereby impairing the performance of the solution in terms of cleaning and oxide formation. This is due to the formation of carbonates in the solution.

Aqueous alkaline solutions are known. For example, DE 1546162 A1 discloses such a solution for cleaning work pieces of iron, steel, zinc, and alloys thereof.

DE 2507056 A1 discloses a solution for cleaning iron-containing metal pieces.

US 4,720,332 A relates to the chemical stripping of nickel and nickel alloys from metallic and non-metallic substrates utilizing an aqueous alkaline solution.

US 6,036,758 A discloses a composition useful for the surface treatment of copper, in particular for micro-roughening of the copper surface so as to improve the adhesion characteristics of the copper surface, comprises an oxidizing agent for copper and an aromatic sulfonic acid or a salt thereof. However, the solution is strongly acidic and immediately removes any oxides.

OBJECT OF THE INVENTION

The object of the present invention was to provide a method of forming uniform copper oxide on a copper surface, the oxide additionally being quickly obtained, sufficiently thick, and not negatively affected by the presence of carbonate.

SUMMARY OF THE INVENTION

The above object is solved by a method of forming copper oxide on a copper surface, the method comprising the steps

- a) providing a substrate comprising the copper surface,
- b) optionally pre-cleaning the copper surface,
- c) contacting the copper surface with an alkaline aqueous oxidizing solution comprising one or more than one oxidizing compound selected from the group consisting of
 - an aromatic sulfonic acid compound, salts thereof,
 - an aromatic sulfonic acid ester compound, salts thereof,
 - an aromatic nitro compound, and salts thereof,

such that said copper oxide is formed on the copper surface.

Preferred embodiments are defined in dependent claims and disclosed in the following specification.

The present invention furthermore relates to a use of an oxidizing compound selected from the group consisting of

- an aromatic sulfonic acid compound, salts thereof,
- an aromatic sulfonic acid ester compound, salts thereof,
- an aromatic nitro compound, and salts thereof,

in an alkaline aqueous oxidizing solution to form uniform copper oxide on a copper surface.

Own experiments have shown that one or more, preferably all of the following beneficial effects are achieved by the method of the present invention or a preferred embodiment thereof:

- formation of sufficiently thick copper oxide (typically a layer of copper(II)oxide) on the copper surface in a reasonable contacting time, such as up to 20 $\mu\text{g}/\text{cm}^2$ within a few minutes,
- formation of uniform copper oxide,
- formation of copper oxide is quickly initiated after contacting, i.e. without adverse delay, which allows optimization of existing manufacturing processes,

- a presence of carbon dioxide has less or no adverse effect on the performance of the aqueous alkaline oxidizing solution or on above-mentioned beneficial effects, such that also an aged oxidizing solution performs well,
- ideally transportation of impurities present on the copper surface into the copper oxide to additionally increase cleaning performance.

DETAILED DESCRIPTION OF THE INVENTION

In the method of the present invention a uniform copper oxide is formed on the copper surface. In the context of the present invention, "uniform" denotes a highly homogeneous copper oxide with a substantially constant thickness and a regular/even copper oxide surface. Therefore, the method of the present invention preferably is a method of forming uniform copper oxide on a copper surface.

Step a), providing the substrate:

In step a) of the method of the present invention, a substrate comprising the copper surface is provided. Most preferably, the copper surface is the surface of a copper deposit, preferably of a copper layer. The copper deposit and the copper layer, respectively, preferably comprises 95 atom% or more copper, based on the total number of atoms in the copper deposit and the copper layer, respectively, more preferably 97 atom% or more, even more preferably 99 atom% or more, most preferably is pure metallic copper. This preferably applies likewise to the copper surface. Thus, in some cases a method of the present invention is preferred, wherein the copper surface comprises, in tiny amounts, elements other than copper.

Preferred is a method of the present invention, wherein in step a) the substrate comprising the copper surface is or comprises a non-conductive substrate, preferably is or comprises a resin, a glass, a ceramic, a plastic, a wafer, or combinations thereof, even more preferably the substrate is or comprises a resin, most preferably is or comprises an epoxy resin.

Preferred is a method of the present invention, wherein in step a) the substrate does not comprise a surface of iron and of tin, preferably does not comprise at all iron and tin.

Preferably, the substrate is an electronic article, a part, or a pre-product thereof or is a substrate finally resulting in an electronic article, a part, or a product thereof.

Preferred is a method of the present invention, wherein the copper surface is a patterned copper surface, most preferably a patterned copper layer. In the context of the present invention "patterned" includes structured, i.e. the copper surface has a three dimensional surface. Thus in

some cases it is preferred that the copper surface is patterned, wherein in other cases the copper surface is a copper layer; preferred is in many cases a patterned copper surface.

Step b), pre-cleaning the copper surface:

In a preferred embodiment of the method of the present invention, the method comprises prior to step c):

step b) pre-cleaning the copper surface.

Generally, step b) is optional. However, in many cases a method of the present invention is preferred, wherein the method includes said pre-cleaning.

In the context of the present invention, "pre-cleaning" means removal of impurities from the copper surface. Impurities are preferably all other substances than metallic copper. Thus, pre-cleaning preferably means to bring the copper surface in a condition that the surface solely or predominantly comprises metallic copper, i.e. Cu^0 , prior to step c) of the method of the present invention.

Preferred is a method of the present invention, wherein the pre-cleaning in step b) is done by contacting the copper surface with an aqueous pre-cleaning solution comprising an oxidizing compound different from those defined in step c), and wherein the pre-cleaning solution has a pH of ≤ 4 .

Preferred is a method of the present invention, wherein in the pre-cleaning solution the oxidizing compound comprises one or more than one peroxide, preferably one or more than one peroxodisulfate. Preferably, in the pre-cleaning solution a peroxide, preferably the one or more than one peroxodisulfate, is the only non-metallic oxidizing compound.

Preferred is a method of the present invention, wherein in the pre-cleaning solution the oxidizing compound has a total concentration in a range from 0.1 mol/L to 1.5 mol/L, based on the total volume of the pre-cleaning solution, preferably in a range from 0.2 mol/L to 1.2 mol/L, more preferably in a range from 0.3 mol/L to 1.0 mol/L, even more preferably in a range from 0.4 mol/L to 0.9 mol/L, most preferably in a range from 0.5 mol/L to 0.7 mol/L. The aforementioned concentrations are preferably applicable to aforementioned preferred peroxides, most preferably to peroxodisulfates.

Preferred is a method of the present invention, wherein in step b) the pre-cleaning solution has a pH of ≤ 4 , preferably a pH in a range from -2.0 to 4.0, more preferably in a range from -1.0 to 3.9, even more preferably in a range from 0 to 3.8. In such an acidic environment, impurities

such as undesired copper oxide are removed to obtain a sufficiently cleansed metallic copper surface prior to step c).

Preferred is a method of the present invention, wherein in step b) the pre-cleaning is carried out by spraying, dipping or rinsing.

Step c), contacting with an alkaline aqueous oxidizing solution:

The oxidizing solution utilized in step c) of the method of the present invention is an alkaline aqueous solution. In the context of the present invention, "aqueous" denotes that the oxidizing solution comprises water. Preferred is an oxidizing solution utilized in the method of the present invention, wherein more than 50 vol% of the total volume of the oxidizing solution is water, preferably 70 vol% or more, more preferably 80 vol% or more, even more preferably 90 vol% or more, most preferably 95 vol% or more. Most preferably, the oxidizing solution comprises water with the proviso that water is the only solvent.

The term "alkaline" means that the oxidizing solution has a pH of more than 7, preferably of 9 or more, even more preferably of 11 or more, most preferably of 12.5 or more. Preferred is an oxidizing solution in step c) of the method of the present invention, wherein the pH is in a range from 8 to 14, more preferably in a range from 9 to 14, even more preferably in a range from 10 to 14, yet even more preferably in a range from 11 to 14, most preferably in a range from 12 to 14. If the pH is insufficiently alkaline, the copper oxide will dissolve, which is undesired. It is the objective of the present invention to form and to maintain the copper oxide during step c) of the method of the present invention.

In order to obtain an alkaline pH, the oxidizing solution comprises hydroxide ions, preferably in a concentration in a range from 0.1 mol/L to 2.0 mol/L, based on the total volume of the oxidizing solution, preferably in a range from 0.2 mol/L to 1.8 mol/L, even more preferably in a range from 0.3 mol/L to 1.6 mol/L, yet even more preferably in a range from 0.4 mol/L to 1.5 mol/L, most preferably in a range from 0.5 mol/L to 1.2 mol/L. Such concentrations result in a preferably strong alkaline oxidizing solution, e.g. pH 13 or higher.

Preferred is an oxidizing solution comprising one or more than one source of hydroxide ions, preferably one source of hydroxide ions.

A preferred source of hydroxide ions is an inorganic hydroxide, an organic hydroxide, or mixtures thereof. An inorganic hydroxide is preferably selected from the group consisting of ammonium hydroxide and alkaline hydroxides, is preferably selected from the group consisting of ammonium hydroxide, sodium hydroxide, and potassium hydroxide. A preferred organic hydrox-

ide is an alkyl ammonium hydroxide, preferably tetra alkyl ammonium hydroxide, more preferably tetra methyl ammonium hydroxide.

In step c) of the method of the present invention, contacting is preferably carried out by spraying, dipping or rinsing, such that the copper surface is partly or entirely in contact with the oxidizing solution.

Preferred is a method of the present invention, wherein in step c) the copper surface has a (substantially) horizontal or (substantially) vertical orientation. This addresses typical process designs common in manufacturing respective electronic devices, namely a respective vertical and horizontal process. In a horizontal process, the copper surface is oriented horizontally, or substantially horizontally when contacted with the oxidizing solution. In such a case, step c) is preferably carried out by spraying the oxidizing solution on the copper surface. In a vertical process, the copper surface is oriented vertically, or substantially vertically when contacted with the oxidizing solution. In such a case, step c) is preferably carried out by immersing the copper surface into the oxidizing solution.

Oxidizing compound:

In step c) of the method of the present invention, the alkaline aqueous oxidizing solution comprises one or more than one, preferably one, oxidizing compound selected from the group consisting of

- an aromatic sulfonic acid compound, salts thereof,
- an aromatic sulfonic acid ester compound, salts thereof,
- an aromatic nitro compound, and salts thereof.

Thus, the formed copper oxide is directly a result of an oxidation caused by said oxidizing compound in the alkaline aqueous oxidizing solution. This also means that the alkaline aqueous oxidizing solution has its oxidizing capacities as a result of the presence of said one or more than one, preferably one, oxidizing compound.

The aromatic sulfonic acid compound comprises one or more than one, preferably one, sulfonic acid group. The aromatic sulfonic acid ester compound comprises one or more than one, preferably one, esterified sulfonic acid group.

Each above mentioned aromatic compound comprises at least one aromatic ring. Preferred is an oxidizing solution, wherein each aromatic compound comprises only one aromatic ring, preferably only one aromatic ring with only carbon ring atoms. This means that the oxidizing solu-

tion preferably does not comprise a hetero-aromatic compound, most preferably no hetero-aromatic compound is utilized in the method of the present invention. Preferably, said aromatic compounds comprise a benzene moiety, most preferably the only one aromatic ring is a benzene moiety.

Preferred salts of said aromatic compounds are alkali metal salts and ammonium salts, preferably sodium and potassium salts.

In some cases it is preferred that said aromatic compounds are substituted with one or more than one substituent, wherein the one or more than one substituent is connected with the at least one aromatic ring and/or with the sulfonic acid group. Preferred substituents are selected from the group consisting of nitro group, sulfonic acid group, alkoxy group, halogen group, and alkyl group. More preferably, substituents are selected from the group consisting of nitro group, sulfonic acid group, alkoxy group, halogen group, and alkyl group, with the proviso that the aromatic nitro compound, and salts thereof is not substituted with a sulfonic acid group. Thus, the aromatic nitro compound and salts thereof is preferably free of a sulfonic acid group, more preferably is free of sulfur.

A preferred alkyl group is a C1 to C6 alkyl group, preferably C1 to C4, more preferably C1 to C3.

A preferred halogen group is chloride and bromide. In some cases it is preferred that the one or more than one oxidizing compound comprises a $-\text{SO}_2\text{Cl}$ group. This is a preferred representative of a substituted aromatic compound, preferably of a substituted aromatic sulfonic acid compound.

A preferred alkoxy group is C1 to C3 alkoxy, preferably methoxy. In some cases it is preferred that the one or more than one oxidizing compound comprises a $-\text{SO}_2\text{OCH}_3$ group. This is a preferred representative of a substituted aromatic compound, preferably of a substituted aromatic sulfonic acid compound.

A preferred substituent for the aromatic sulfonic acid compound, salts thereof, the aromatic sulfonic acid ester compound, and salts thereof is a nitro group, most preferably for the aromatic sulfonic acid compound and salts thereof. Preferred is a method of the present invention, wherein in step c)

- the aromatic sulfonic acid compound and salts thereof comprise one or more than one (preferably one) nitro group, preferably at least one nitro group being directly attached to an aromatic ring,

and/or

- the aromatic sulfonic acid ester compound and salts thereof comprise one or more than one (preferably one) nitro group, preferably at least one nitro group being directly attached to an aromatic ring.

Preferred is a method of the present invention, wherein in step c) the aromatic nitro compound and salts thereof comprises nitro benzene, salts thereof, substituted nitro benzene and/or salts thereof, preferably nitro benzene and salts thereof. The substituted nitro benzene and salts thereof comprise a substituent, preferably as defined above, preferably with the proviso that the substituted nitro benzene and salts thereof is free of a sulfonic acid group, more preferably is free of sulfur.

Preferred is a method of the present invention, wherein in step c) the one or more than one oxidizing compound selected from the group consisting of

- an aromatic sulfonic acid compound, salts thereof,
- an aromatic sulfonic acid ester compound, salts thereof,
- an aromatic nitro compound, and salts thereof,

constitutes a total molar amount of 96 mol% or more of all aromatic compounds in the oxidizing solution, preferably 97 mol% or more, more preferably 98 mol% or more, even more preferably 99 mol% or more, most preferably is the only aromatic compound in the oxidizing solution,

and/or

the one or more than one oxidizing compound selected from the group consisting of

- an aromatic sulfonic acid compound, salts thereof,
- an aromatic sulfonic acid ester compound, salts thereof,
- an aromatic nitro compound, and salts thereof,

constitutes a total molar amount of 96 mol% or more of all oxidizing compounds in the oxidizing solution to oxidize the copper surface, preferably 97 mol% or more, more preferably 98 mol% or more, even more preferably 99 mol% or more, most preferably is the only oxidizing compound, except dissolved molecular oxygen, in the oxidizing solution.

Preferably, the dissolved molecular oxygen is oxygen from ambient air, typically in little concentrations. This oxygen usually dissolves unavoidably in the oxidizing solution.

Preferred is a method of the present invention, wherein in step c) the oxidizing solution comprises substituted benzene sulfonic acid and/or salts thereof, and preferably 96 mol% or more of all aromatic compounds in the oxidizing solution is substituted benzene sulfonic acid and salts thereof, more preferably 97 mol% or more, even more preferably 98 mol% or more, most preferably 99 mol% or more.

Preferred is a method of the present invention, wherein in step c) the oxidizing solution comprises nitrobenzene sulfonic acid and/or salts thereof, and preferably 96 mol% or more of all aromatic compounds in the oxidizing solution is nitrobenzene sulfonic acid and salts thereof, more preferably 97 mol% or more, even more preferably 98 mol% or more, most preferably 99 mol% or more. The nitro group is preferably in ortho, meta, or para position, most preferably in meta position.

Preferred is in step c) an oxidizing solution, wherein said one or more than one oxidizing compound has a total concentration in a range from 5 mmol/L to 500 mmol/L, based on the total volume of the oxidizing solution, preferably in a range from 10 mmol/L to 400 mmol/L, more preferably in a range from 15 mmol/L to 300 mmol/L, even more preferably in a range from 20 mmol/L to 200 mmol/L, yet even more preferably in a range from 25 mmol/L to 100 mmol/L, most preferably in a range from 30 mmol/L to 70 mmol/L. This means that if more than one of these compounds is present, the concentration relates to the total concentration of all these compounds. This preferably applies with the proviso that said one or more than one oxidizing compound is the only oxidizing compound, except dissolved molecular oxygen, in the oxidizing solution.

More preferred is in step c) an oxidizing solution, comprising one or more than one, preferably one, oxidizing compound selected from the group consisting of an aromatic sulfonic acid compound and salts thereof (preferably a substituted benzene sulfonic acid compound and salts thereof), wherein said one or more than one oxidizing compound preferably has a total concentration in a range from 5 mmol/L to 500 mmol/L, based on the total volume of the oxidizing solution, preferably in a range from 10 mmol/L to 400 mmol/L, more preferably in a range from 15 mmol/L to 300 mmol/L, even more preferably in a range from 20 mmol/L to 200 mmol/L, yet even more preferably in a range from 25 mmol/L to 100 mmol/L, most preferably in a range from 30 mmol/L to 70 mmol/L. This preferably applies with the proviso that said one or more than one oxidizing compound is the only oxidizing compound, except dissolved molecular oxygen, in the oxidizing solution.

Most preferred is in step c) an oxidizing solution, comprising one or more than one, preferably one, oxidizing compound selected from the group consisting of a nitrobenzene sulfonic acid and salts thereof, wherein said one or more than one oxidizing compound preferably has a total concentration in a range from 5 mmol/L to 500 mmol/L, based on the total volume of the oxidizing solution, preferably in a range from 10 mmol/L to 400 mmol/L, more preferably in a range from 15 mmol/L to 300 mmol/L, even more preferably in a range from 20 mmol/L to 200 mmol/L, yet even more preferably in a range from 25 mmol/L to 100 mmol/L, most preferably in a range from 30 mmol/L to 70 mmol/L. This preferably applies with the proviso that said one or more than one oxidizing compound is the only oxidizing compound, except dissolved molecular oxygen, in the oxidizing solution. Nitrobenzene sulfonic acid and salts thereof are very preferred oxidizing compounds. The nitro group is preferably in ortho, meta, or para position, most preferably in meta position.

Yet most preferred is an oxidizing solution, comprising as the one or more than one oxidizing compound 3-nitrobenzene sulphonic acid and/or salts thereof, preferably 3-nitrobenzene sulphonic acid and/or salts thereof is the only oxidizing compound, except dissolved molecular oxygen, in the oxidizing solution, preferably in a total concentration in a range from 5 mmol/L to 500 mmol/L, based on the total volume of the oxidizing solution, preferably in a range from 10 mmol/L to 400 mmol/L, more preferably in a range from 15 mmol/L to 300 mmol/L, even more preferably in a range from 20 mmol/L to 200 mmol/L, yet even more preferably in a range from 25 mmol/L to 100 mmol/L, most preferably in a range from 30 mmol/L to 70 mmol/L.

Preferred is an oxidizing solution, wherein the aromatic sulfonic acid ester compound and salts thereof is an alkyl ester, preferably independently a methyl-ester, ethyl-ester or propyl ester. If more than one sulfonic acid group is present, one or more than one is esterified.

Further compounds in the oxidizing solution:

In some cases a method of the present invention is preferred, wherein in step c) the oxidizing solution additionally comprises one or more than one complexing agent. The complexing agent typically serves to complex copper ions that are solubilized when applying the oxidizing solution on the copper surface, which avoids formation of insoluble copper hydroxides. Typically, a complexing agent for copper ions prevents or at least significantly reduces such hydroxide formation. Thus, preferred is a method of the present invention, wherein in step c) the oxidizing solution additionally comprises one or more than one complexing agent for complexing copper ions, preferably one or more than one complexing agent comprising at least one carboxylic group and at least one hydroxyl group.

More preferred is a method of the present invention, wherein in the oxidizing solution the one or more than one complexing agent comprises a sugar, preferably a monomeric sugar.

Even more preferred is a method of the present invention, wherein the one or more than one complexing agent for complexing copper ions comprises gluconic acid and/or salts thereof, most preferably the only complexing agent for complexing copper ions in the oxidizing solution is gluconic acid and/or salts thereof.

Preferred is a method of the present invention, wherein in the oxidizing solution the one or more than one complexing agent has a total concentration in a range from 5 mmol/L to 400 mmol/L, based on the total volume of the oxidizing solution, preferably in a range from 10 mmol/L to 300 mmol/L, more preferably in a range from 15 mmol/L to 200 mmol/L, even more preferably in a range from 20 mmol/L to 100 mmol/L, yet even more preferably in a range from 25 mmol/L to 80 mmol/L, most preferably in a range from 30 mmol/L to 60 mmol/L. The aforementioned concentrations are preferably applicable to aforementioned preferred complexing agents, most preferably to gluconic acid and salts thereof.

Preferred is a method of the present invention, wherein the oxidizing solution is substantially free of or does not comprise benzimidazole, preferably is substantially free of or does not comprise an azole.

Preferred is a method of the present invention, wherein the oxidizing solution is substantially free of or does not comprise a polyethylene compound, preferably is substantially free of or does not comprise a polyalkylene compound.

Preferred is a method of the present invention, wherein the oxidizing solution is substantially free of or does not comprise a surfactant.

Preferred is a method of the present invention, wherein the oxidizing solution is substantially free of or does not comprise hydrogen peroxide, more preferably is substantially free of or does not comprise a peroxide. In many cases such a too strong oxidizing compound generates an undesired needle-type copper oxide in an insufficient uniform copper oxide layer.

Preferred is a method of the present invention, wherein the oxidizing solution is substantially free of or does not comprise chlorite ions, preferably is substantially free of or does not comprise chlorite ions and hypochlorite ions, most preferably is substantially free of or does not comprise chlorine-oxygen anions.

Preferred is a method of the present invention, wherein the oxidizing solution is substantially free of or does not comprise hypophosphite ions.

Preferred is a method of the present invention, wherein in step c) the time period for the contacting with the oxidizing solution is in a range from 3 seconds to ≤ 5 minutes, preferably in a range from 4 seconds to ≤ 4 minutes, more preferably in a range from 5 seconds to ≤ 3 minutes, even more preferably in a range from 6 seconds to ≤ 2 minutes, most preferably in a range from 7 seconds to ≤ 1 minute.

Preferred is a method of the present invention, wherein in step c) the temperature of the oxidizing solution is in a range from 20°C to 80°C, preferably in a range from 25°C to 75°C, more preferably in a range from 30°C to 70°C, even more preferably in a range from 35°C to 65°C, most preferably in a range from 40°C to 60°C.

Preferred is a method of the present invention, wherein after step c) copper oxide is formed on the copper surface in an amount in a range from 10 - 50 $\mu\text{g}/\text{cm}^2$, preferably in a range from 11 - 45 $\mu\text{g}/\text{cm}^2$, more preferably in a range from 12 - 40 $\mu\text{g}/\text{cm}^2$, even more preferably in a range from 13 - 35 $\mu\text{g}/\text{cm}^2$, most preferably in a range from 14 - 32 $\mu\text{g}/\text{cm}^2$.

Preferred is a method of the present invention, wherein after step c) the copper oxide forms a uniform copper oxide layer, preferably with a layer thickness in the range from 4 nm to 100 nm, based on copper-(II)-oxide, preferably in a range from 5 nm to 80 nm, more preferably in a range from 6 nm to 60 nm.

Preferred is a method of the present invention, wherein the copper oxide formed on the copper surface is substantially free of or does not comprise needle-type copper oxide. Furthermore, preferred is a method of the present invention, wherein the copper oxide formed on the copper surface is (substantially) not a copper oxide corresponding to black oxide.

A method of the present invention is preferred, wherein after step c) the copper oxide (i) is removed in an additional step or (ii) is maintained and not removed in an additional step.

In some cases a method of the present invention is preferred, comprising further after step c):

d) removing the copper oxide, preferably by contacting the copper oxide with an acidic solution.

After step d), typically a very thoroughly cleansed copper surface is obtained.

Use and product:

The present invention also relates to a use of an oxidizing compound selected from the group consisting of

- an aromatic sulfonic acid compound, salts thereof,
- an aromatic sulfonic acid ester compound, salts thereof,
- an aromatic nitro compound, and salts thereof,

in an alkaline aqueous oxidizing solution to form uniform copper oxide on a copper surface. The aforementioned regarding the method of the present invention preferably applies likewise to the use of the present invention.

The present invention preferably also relates to a product obtained or obtainable by the method of the present invention. The product preferably has the properties indicated above. The aforementioned regarding the method of the present invention preferably applies likewise to the product of the present invention.

Preferably, the product of the present invention is an electronic article, preferably a printed circuit board or a wafer.

EXAMPLES

A) Oxidizing solutions:

Alkaline aqueous oxidizing solution of the present invention:

An oxidizing solution of the present invention (hereinafter simply named "inv") is produced by adding 10 mmol/L to 50 mmol/L 3-nitrobenzene sulphonate as oxidizing compound to an alkaline aqueous solution comprising between 0.5 mol/L and 1 mol/L NaOH (pH 13 to 14) and gluconate as complexing agent.

Alkaline aqueous oxidizing solution (comparative 1):

For comparative reasons, a solution is prepared as described above for "inv" but without 3-nitrobenzene sulphonate (hereinafter simply named "comp 1"). In this solution oxidation of copper to form copper oxide is primarily facilitated by means of dissolved ambient air oxygen in a strong alkaline solution.

Non-alkaline (acidic) aqueous oxidizing solution (comparative 2):

A non-alkaline oxidizing solution comprising between 0.4 mol/L and 0.6 mol/L H₂O₂ in an aqueous solution having a pH in a range from 4.0 to 4.5 is also prepared for comparative reasons (hereinafter simply named "comp 2"). In this solution oxidation of copper to form copper oxide is

primarily facilitated by means of H_2O_2 , wherein the pH is not too acidic in order to avoid severe dissolution of the formed copper oxide.

B) Experiments

Experiments are carried out in order to test the following characteristics:

- (i) optical appearance after step c),
- (ii) initiation time of copper oxide formation,
- (iii) amount of formed copper oxide,
- (iv) homogeneity of formed copper oxide,
- (v) copper oxide formation (determined by oxide weight gain) in the presence of different carbonate concentrations

According to step a) of the method of the present invention, copper clad laminates (CCL, EM-825(I), Elite Material Co., Ltd.; 35 μ m copper foil on a non-conductive resin, 7.5 cm x 15 cm) comprising a copper surface, are provided as substrates for the respective experiments.

According to step b) of the method of the present invention, the copper surface is pre-cleaned in an aqueous pre-cleaning solution (35°C) comprising sodium peroxydisulfate (SPS), sulfuric acid, and copper sulfate followed by a rinsing step with water. As a result, a pre-cleansed copper surface is obtained exhibiting a pure metallic copper surface.

According to step c) of the method of the present invention, the pre-cleansed copper surface is contacted with the respective oxidizing solution at 50°C for 3 minutes contacting time ("inv" and "comp1") or at 35°C for 1 minute contacting time ("comp2"). Characteristics (i) to (iv) are determined afterwards. A summary of the results is provided in Table A below.

In order to test characteristic (v), in one set of experiments the oxidizing solutions "inv" and "comp1" are artificially carbonized by directly introducing gaseous CO_2 to finally obtain pre-determined carbonate concentrations (volumetric flow-rate approximately 0.5 L/min). For that an almost complete carbonization of the contained hydroxides is carried out. Afterwards, the desired concentration of carbonate is pH-metrical titrated and carefully checked before each experiment is carried out. In this way the naturally occurring carbonization facilitated by carbon dioxide from ambient air is simulated. The oxide weight gain (incorporation of oxide) is determined depending on the concentration of carbonate. Results are obtained for 3 minutes and 5 minutes contacting time, respectively, in step c). The following carbonate concentrations in g/L

are tested: 0 (reference), 5, 15, and 30, based on the total amount of carbonate and hydrogen carbonate in the respective oxidizing solution. This simulates natural aging of an alkaline aqueous oxidizing solution, which typically is a result from carbon dioxide absorption by ambient air. This simulation allows evaluating whether the advantageous formation of copper oxide still occurs in such an aged oxidizing solution. The results are summarized in Table B below.

After step c), each substrate is rinsed with water and dried at approximately 65°C.

C. Results and Summary

Results of characteristics (i) to (iv) are summarized in following Table A

Table A: Results of characteristics (i) to (iv)

	Characteristic			
Sample	(i), visual inspection	(ii) in [s]	(iii) in [$\mu\text{g}/\text{cm}^2$]	(iv)*
"inv"	Golden/greenish tint	10	18	+++
"comp1"	Dull copper color	25	6	+
"comp2"	Orange	4	n.d.	++

* "+++" denotes high homogeneity, "++" acceptable homogeneity, "+" inhomogeneous, conclusion based on (i)

n.d. denotes not determined

Table B: Results of copper oxide formation in the presence of carbonate for "inv" and "comp1"

Characteristic (i) and (iii) dependent on different carbonate concentrations				
	"inv", 3 minutes contacting time			
	0 g/L**	5 g/L	15 g/L	30 g/L
(i)	Golden/greenish tint	Golden/greenish tint	Golden/greenish tint	Dull copper color
(iii) [$\mu\text{g}/\text{cm}^2$]	18	17	19	14
	"inv", 5 minutes contacting time			
(i)	Golden/greenish tint	Golden/greenish tint	Golden/greenish tint	Golden/greenish tint

(iii) [μg/cm ²]	29	30	29	18
	"comp1", 3 minutes contacting time			
(i)	Dull copper color	copper color	hazy copper color	Copper color
(iii) [μg/cm ²]	6	6	5	9
	"comp1", 5 minutes contacting time			
(i)	Dull copper color	hazy copper color	hazy copper color	Brownish copper color
(iii) [μg/cm ²]	9	9	6	12

** carbonate concentration

To the characteristics in detail:

To (i):

A copper surface contacted with "inv" results in a copper oxide with a significant golden color with a greenish tint (see Table A). This color is characteristic for the method of the present invention and is basically still formed in an even aged oxidizing solution unless comparatively high carbonate concentrations are reached (see Table B, "inv", 3 minutes contacting time, 30 g/L carbonate concentration). With 3 minutes contacting time, the characteristic color is maintained for a carbonate concentration from 0 g/L to at least 15 g/L. In contrast, if the contacting time is 5 minutes, the characteristic color is even maintained including a carbonate concentration of 30 g/L (see Table B, "inv", 5 minutes contacting time).

However, a copper surface contacted with "comp1" results in a copper oxide with an undefined copper color including a dull and/or hazy appearance.

This color difference allows a simple optical inspection of copper surfaces treated according to the method of the present invention and easily indicates that the desired copper oxide is present.

A substrate contacted with "comp2" shows a strong orange color, which is not further investigated in the presence of carbonate. Although oxidation with H₂O₂ is comparatively quick (4 seconds) several disadvantages are clearly observed in our experiments:

- copper oxide unacceptably dissolves in the weakly acid oxidizing solution; although the pH is only weakly acidic, undesired dissolution cannot be fully excluded in this step
- the undesired dissolution of copper oxide increases the concentration of copper ions in the oxidizing solution significantly more than in oxidizing solution “inv” and “comp1”, which is not desired and thus requires comparatively high concentrations of a complexing agent for copper ions
- the H_2O_2 -concentration in “comp2” is not stable because “comp2” preferably requires a more acidic pH in order to stabilize H_2O_2 , which, however, is detrimental in view of copper oxide stability; thus the long-time stability of “comp2” is negatively affected

To (ii):

Table A shows that the formation of copper oxide upon contacting with “inv” is initiated significantly earlier compared to contacting with “comp1”. Thus, “inv” significantly accelerates the initiation of copper oxide formation and significantly lowers the initiation time compared to “comp1”.

In contrast, contacting with “comp2” results in the quickest initiation of copper oxide formation (only 4 seconds). However, over time for “comp2” this value significantly changes due to undesired copper ion dissolution (data not shown). Such significant changes are not observed for “inv” and “comp1” over time.

To (iii):

Table A shows that contacting with “inv” results in an increased amount of formed copper oxide, which is approximately tripled compared to contacting with “comp1” (compare Table A, “comp1”, 6 $\mu\text{g}/\text{cm}^2$ vs. “inv”, 18 $\mu\text{g}/\text{cm}^2$). Furthermore, Table B shows that in each case more copper oxide is formed upon contacting with “inv” compared to contacting with “comp1”.

To (iv):

Homogeneity was determined by visual inspection. A uniformly distributed color (without darker/brighter areas, spots, blurs and stains) indicates a uniform copper oxide layer. In contrast, a surface with darker/brighter areas of a color including spots, blurs and stains strongly indicates an oxide layer with significantly varying thickness and an obvious inhomogeneity.

In each case, upon contacting with “inv” homogeneity was considerably improved compared to contacting with “comp1”. Contacting with “inv” results in a uniformly distributed golden color with a greenish tint, even in the presence of carbonate. This means that the copper surface is equal-

ly and uniformly oxidized over the entire copper surface such that a very uniform and highly homogeneous copper oxide is obtained.

In contrast, contacting with “comp1” results in an inhomogeneous copper oxide layer, characterized by a not uniformly distributed color (including a dull and/or hazy appearance). The same inhomogeneity for “comp1” is observed in the presence of carbonate.

To (v):

Table B shows that, in each case, a contacting with “inv” results in a formation of copper oxide. Furthermore, in each case the amount of formed copper oxide is higher compared to a contacting with “comp1”. As a result, formation of copper oxide is not negatively affected by the presence of carbonate and increased copper oxide formation also occurs in aged oxidizing solutions.

CLAIMS

1. A method of forming copper oxide on a copper surface, the method comprising the steps
 - a) providing a substrate comprising the copper surface,
 - b) optionally pre-cleaning the copper surface,
 - c) contacting the copper surface with an alkaline aqueous oxidizing solution comprising one or more than one oxidizing compound selected from the group consisting of
 - an aromatic sulfonic acid compound, salts thereof,
 - an aromatic sulfonic acid ester compound, salts thereof,
 - an aromatic nitro compound, and salts thereof,such that said copper oxide is formed on the copper surface.
2. The method of claim 1, wherein the pre-cleaning in step b) is done by contacting the copper surface with an aqueous pre-cleaning solution comprising an oxidizing compound different from those defined in step c), and wherein the pre-cleaning solution has a pH of ≤ 4 .
3. The method of claim 2, wherein the oxidizing compound comprises one or more than one peroxide, preferably one or more than one peroxodisulfate.
4. The method of any of the preceding claims, wherein in step c)
 - the aromatic sulfonic acid compound and salts thereof comprise one or more than one nitro group, preferably at least one nitro group being directly attached to an aromatic ring, and/or
 - the aromatic sulfonic acid ester compound and salts thereof comprise one or more than one nitro group, preferably at least one nitro group being directly attached to an aromatic ring.
5. The method of any of the preceding claims, wherein in step c) the aromatic nitro compound and salts thereof comprises nitro benzene, salts thereof, substituted nitro benzene and/or salts thereof, preferably nitro benzene and salts thereof.
6. The method of any of the preceding claims, wherein in step c) the one or more than one oxidizing compound selected from the group consisting of
 - an aromatic sulfonic acid compound, salts thereof,

- an aromatic sulfonic acid ester compound, salts thereof,
- an aromatic nitro compound, and salts thereof,

constitutes a total molar amount of 96 mol% or more of all aromatic compounds in the oxidizing solution, preferably 97 mol% or more, more preferably 98 mol% or more, even more preferably 99 mol% or more, most preferably is the only aromatic compound in the oxidizing solution,

and/or

the one or more than one oxidizing compound selected from the group consisting of

- an aromatic sulfonic acid compound, salts thereof,
- an aromatic sulfonic acid ester compound, salts thereof,
- an aromatic nitro compound, and salts thereof,

constitutes a total molar amount of 96 mol% or more of all oxidizing compounds in the oxidizing solution to oxidize the copper surface, preferably 97 mol% or more, more preferably 98 mol% or more, even more preferably 99 mol% or more, most preferably is the only oxidizing compound, except dissolved molecular oxygen, in the oxidizing solution.

7. The method of any of the preceding claims, wherein in step c) the oxidizing solution comprises nitrobenzene sulfonic acid and/or salts thereof, and preferably 96 mol% or more of all aromatic compounds in the oxidizing solution is nitrobenzene sulfonic acid and salts thereof, more preferably 97 mol% or more, even more preferably 98 mol% or more, most preferably 99 mol% or more.
8. The method of any of the preceding claims, wherein in step c) the time period for the contacting with the oxidizing solution is in a range from 3 seconds to ≤ 5 minutes, preferably in a range from 4 seconds to ≤ 4 minutes, more preferably in a range from 5 seconds to ≤ 3 minutes, even more preferably in a range from 6 seconds to ≤ 2 minutes, most preferably in a range from 7 seconds to ≤ 1 minute.
9. The method of any of the preceding claims, wherein in step c) the temperature of the oxidizing solution is in a range from 20°C to 80°C, preferably in a range from 25°C to 75°C, more preferably in a range from 30°C to 70°C, even more preferably in a range from 35°C to 65°C, most preferably in a range from 40°C to 60°C.

10. The method of any of the preceding claims, wherein in step c) the oxidizing solution additionally comprises one or more than one complexing agent for complexing copper ions, preferably one or more than one complexing agent comprising at least one carboxylic group and at least one hydroxyl group.
11. The method of claim 10, wherein the one or more than one complexing agent for complexing copper ions comprises gluconic acid and/or salts thereof, most preferably the only complexing agent for complexing copper ions in the oxidizing solution is gluconic acid and/or salts thereof.
12. The method of any of the preceding claims, wherein in step a) the substrate comprising the copper surface is or comprises a non-conductive substrate, preferably is or comprises a resin, a glass, a ceramic, a plastic, a wafer, or combinations thereof, even more preferably the substrate is or comprises a resin, most preferably is or comprises an epoxy resin.
13. The method of any of the preceding claims, wherein in step a) the substrate does not comprise a surface of iron and of tin, preferably does not comprise at all iron and tin.
14. The method of any of the preceding claims, wherein after step c) copper oxide is formed on the copper surface in an amount in a range from 10 - 50 $\mu\text{g}/\text{cm}^2$, preferably in a range from 11 - 45 $\mu\text{g}/\text{cm}^2$, more preferably in a range from 12 - 40 $\mu\text{g}/\text{cm}^2$, even more preferably in a range from 13 - 35 $\mu\text{g}/\text{cm}^2$, most preferably in a range from 14 - 32 $\mu\text{g}/\text{cm}^2$.
15. The method of any of the preceding claims, wherein in step c) in the alkaline aqueous oxidizing solution said one or more than one oxidizing compound has a total concentration in a range from 5 mmol/L to 500 mmol/L, based on the total volume of the oxidizing solution, preferably in a range from 10 mmol/L to 400 mmol/L, more preferably in a range from 15 mmol/L to 300 mmol/L, even more preferably in a range from 20 mmol/L to 200 mmol/L, yet even more preferably in a range from 25 mmol/L to 100 mmol/L, most preferably in a range from 30 mmol/L to 70 mmol/L.
16. Use of an oxidizing compound selected from the group consisting of
 - an aromatic sulfonic acid compound, salts thereof,
 - an aromatic sulfonic acid ester compound, salts thereof,
 - an aromatic nitro compound, and salts thereof,in an alkaline aqueous oxidizing solution to form uniform copper oxide on a copper surface.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2020/050859

A. CLASSIFICATION OF SUBJECT MATTER

INV. C23C22/63 C23C22/78 C23C22/83 C23C22/58 C23G1/10
H05K3/38

ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C23C C23G H05K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, COMPENDEX, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y A	BE 599 122 A (ROTHSCHILDS CONTINUATION LTD [GB]; N M ROTHSCILD & SONS [GB] ET AL.) 17 July 1961 (1961-07-17) page 1, paragraph 3 - page 2, paragraph 4 page 3, paragraph 2 - page 4, paragraph 2 examples 1-2 claims 1-10	1,4-9, 12,13, 15,16 2,3 10,11,14
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Further documents are listed in the continuation of Box C.



See patent family annex.

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

International application No

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

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