

ETCHANT, REPLENISHMENT SOLUTION AND METHOD FOR PRODUCING COPPER WIRING USING THE SAME

The present invention relates to an etchant and a replenishment
5 solution for copper and copper alloys and a method for producing wirings
using the same.

When a copper wiring is formed by photoetching in course of the
manufacturing of a printed wiring board, iron chloride based etchants,
copper chloride based etchants, alkaline etchants and the like are used for
10 the etchant. These etchants, however, have a problem called undercut in
which copper beneath an etching resist is dissolved. Particularly, in the
case of a finer wiring pattern, the undercut should be minimized.

Conventionally, an etchant for suppressing the undercut has been
examined. For instance, JP 3387528 B proposes an aqueous solution
15 containing: cupric chloride; hydrochloric acid; a 2-aminobenzothiazole based
compound; polyethylene glycol and a polyamine compound.

However, such a conventional etchant is insufficient for suppressing
undercut in some cases, and therefore an etchant with an increased effect
for suppressing undercut is required.

20 Therefore, with the foregoing in mind, it is an object of the present
invention to provide an etchant and a replenishment solution that can
reduce undercut so as to form a fine and dense wiring pattern and a method
for producing a copper wiring using the same.

An etchant of the present invention is an etchant for copper and
25 copper alloys, and includes an aqueous solution containing: 14 to 155 g/liter
of cupric ion source in terms of a concentration of copper ions; 7 to 180
g/liter of hydrochloric acid; and 0.1 to 50 g/liter of azole. The azole includes
nitrogen atoms only as heteroatoms residing in a ring.

A replenishment solution of the present invention is added to the
30 etchant of the present invention when the etchant is used repeatedly. The
replenishment solution includes an aqueous solution containing: 7 to 360
g/liter of hydrochloric acid; and 0.1 to 50 g/liter of azole, the azole including
nitrogen atoms only as heteroatoms residing in a ring.

A method for producing a wiring of the present invention is for
35 etching of copper or copper alloys. The method includes the step of: etching
a portion of a copper layer on an electrical insulative member that is not
covered with an etching resist using the etchant of the present invention so

as to form the wiring.

Fig. 1A and Fig. 1B are cross-sectional views showing a method for producing a wiring of a printed wiring board according to one embodiment of the present invention.

An etchant of the present invention is an acidic type etchant that contains a cupric ion source and hydrochloric acid as main components.

As the cupric ion source, copper chloride, copper hydroxide, copper sulfate, copper bromide, organic acid cuprate and the like are available. Among others, the use of copper chloride (cupric chloride) is preferable because it can increase the stability of an etching rate.

A concentration of the cupric ion source is 14 to 155 g/liter in terms of the concentration of copper ions, preferably 33 to 122 g/liter. In the case of the concentration becoming too low, an etching rate deteriorates. On the other hand, a too-high concentration reduces the tendency to dissolve, which makes an etching rate unstable. In the case of cupric chloride being used as the cupric ion source, a concentration of the cupric chloride is 30 to 330 g/liter, preferably 70 to 260 g/liter.

The etchant of the present invention contains hydrochloric acid. A concentration of the hydrochloric acid is 7 to 180 g/liter, preferably 18 to 110 g/liter. A too-low concentration of hydrochloric acid results in a failure to obtain a stable etching rate, and a too-high concentration degrades the dissolving stability of copper and might cause the generation of reoxidation on a surface of the copper.

In the etchant of the present invention, in order to suppress undercut, azole containing nitrogen atoms only as heteroatoms residing in a ring is added. The azole may be a monocyclic compound or a compound with condensed rings. Among others, an imidazole based compound, a triazole based compound or a tetrazole based compound is preferable, and two or more of these azoles may be combined for the use.

Available imidazole based compounds include: an alkyl imidazole group such as imidazole, 2-methylimidazole, 2-undecyl-4-methylimidazole and 2-phenylimidazole; and a benzimidazole group such as benzimidazole, 2-methylbenzimidazole, 2-undecyl benzimidazole, 2-phenyl benzimidazole and 2-mercaptobenzimidazole, for example. Among them, benzimidazole is preferable.

Available triazole based compounds include: 1,2,3-triazole, 1,2,4-triazole, 5-phenyl-1,2,4-triazole, 5-amino 1, 2, 4-triazole, benzotriazole, 1-methyl-benzotriazole and tolyltriazole, for example. Among them, benzotriazole is preferable.

5 Available tetrazole based compounds include: 1H-tetrazole, 5-amino-1H-tetrazole, 5-methyl-1H-tetrazole, 5-phenyl-1H-tetrazole, 5-mercapto-1H-tetrazole, 1-phenyl-5-mercapto-1H-tetrazole, 1-cyclohexyl-5-mercapto-1H-tetrazole and 5, 5'-bis-1H-tetrazole, for example. Among them, 5-methyl-1H-tetrazole, 5-phenyl-1H-tetrazole and
10 5-amino-1H-tetrazole are preferable. Particularly, 5-phenyl-1H-tetrazole and 5-amino-1H-tetrazole are preferable.

A concentration of the azole is 0.1 to 50 g/liter, preferably 0.1 to 15 g/liter, and more preferably 0.2 to 10 g/liter. A too-low concentration makes the suppression of undercut insufficient and a too-high concentration
15 degrades an etching rate.

The etchant of the present invention may contain at least one selected from the group consisting of a cationic surface active agent, glycol and glycol ether in order to enhance the stability of the solution and to conduct etching uniformly so that the surface configuration after the etching
20 is uniform. As the cationic surface active agent, alkyl-type quaternary ammonium salts such as benzalkonium chloride and alkyltrimethylammonium chloride, for example, are available. As the glycol, ethylene glycol, diethylene glycol, propylene glycol, polyalkylene glycol and the like are available, for example. As the glycol ether,
25 propylene glycol monomethyl ether, ethylene glycol monobutyl ether, 3-methyl-3-methoxybutanol, dipropylene glycol methyl ether, diethylene glycol butyl ether and the like are available, for example.

The etchant of the present invention may contain a solvent other than the above-stated glycol and glycol ether, a surface active agent other
30 than the above-stated cationic surface active agent and various additives as needed.

In order to enhance the stability of the solution and to conduct etching uniformly so that the surface configuration after the etching is uniform, the etchant of the present invention further may include various
35 additives as needed. The additives include: a solvent including alcohols such as methanol, ethanol, 1-propanol, 2-propanol, butanol and benzyl alcohol, amides such as N, N-dimethylformamide, dimethyl imidazolidinon

and N-methyl pyrrolidone and sulfoxides such as dimethyl sulfoxide; anion surface active agents such as fatty acid salt, alkyl sulfate ester salt and alkylphosphate; nonionic surface active agents such as polyoxyethylene alkyl ether, polyoxypropylene alkyl ether and a block polymer of

5 polyoxyethylene and polyoxypropylene; and ampholytic surface active agents including betains such as lauryl dimethyl aminoacetic acid betain, stearyl dimethyl aminoacetic acid betain, lauryl dimethylamine oxide and lauryl hydroxysulfobetain and aminocarboxylic acid.

The etchant of the present invention can be prepared easily by
10 dissolving the above-stated respective components in water. As the water, ion-exchanged water, pure water, ultrapure water and the like whose ionic substances and impurities have been removed are preferable.

A replenishment solution of the present invention is for adding to the etchant of the present invention when the etchant is used repeatedly.
15 The replenishment solution contains 7 to 360 g/liter (preferably, 30 to 360 g/liter) of hydrochloric acid and 0.1 to 50 g/liter (preferably, 0.2 to 30 g/liter) of azole containing nitrogen atoms only as heteroatoms residing in a ring. The replenishment solution added allows the ratio of the respective components in the etchant to be maintained appropriately, whereby a wiring
20 pattern with reduced undercut can be formed stably. The replenishment solution of the present invention further may contain a cupric ion source such as cupric chloride, in which the concentration of the cupric ion source does not exceed 14g/liter in terms of the concentration of copper ions.

A method for using the etchant of the present invention is not
25 limited especially, and available methods include a method of spraying it at a portion of a copper layer on an insulative material that is not covered with an etching resist, and a method of immersing an object to be processed in the etchant. Furthermore, in order to enhance the wettability of the etchant, prior to the processing with the etchant of the present invention, a
30 surface of copper or copper alloys may be wetted in advance with water, hydrochloric acid with a low concentration or the above-stated replenishment solution. Furthermore, air may be blown utilizing bubbling or the like or an oxidant such as hydrogen peroxide may be added in order to restore the etching capability of the etchant by oxidizing cuprous ions,
35 which are generated in the etchant as a result of the etching of copper, to cupric ions. A temperature of the etchant during the etching of copper preferably is 30 to 50°C.

When copper or copper alloys are etched by spraying the etchant of the present invention, preferably, a temperature of the etchant is kept at 30 to 50°C and the spraying is carried out under a spraying pressure of 0.03 to 0.3 MPa. As a result, an etching rate obtained becomes 0.1 to 0.7 $\mu\text{m/s}$,
5 which facilitates the suppression of undercut.

When the etchant of the present invention is used repeatedly, preferably, the etching of copper or copper alloys is carried out while the above-described replenishment solution is added to the etchant so that the concentration of copper ions in the etchant can be kept at 155 g/liter or lower,
10 preferably, at 122 g/liter or lower. This can prevent the deposition of copper crystals. The concentration of copper ions preferably is measured by titration, a conductometric method and the like.

After the etching of copper or copper alloys using the etchant of the present invention, the etched portion preferably is washed with a cleaning
15 fluid that is capable of dissolving the components of the etchant. Thereby, the components of the etchant that remain on a side face of the wirings, for example, can be removed, so that a short-circuit between the wirings, a failure in contact with a solder resist and the like, which result from the residual components, can be prevented. Herein, as the cleaning fluid, at
20 least one solution selected from the group consisting of an acid solution, a solution containing a substance that is capable of forming a complex compound with copper ions and an organic solution is preferable. When the cleaning is carried out with an acid solution or a solution containing a substance that is capable of forming a complex compound with copper ions,
25 the residual components including the cupric ion source (cupric chloride and the like) in the etchant and cuprous chloride and copper oxide generated by the reaction especially can be removed with efficiency. When the cleaning is carried out with an organic solution, the residual components of azole in the etchant especially can be removed with efficiency.

30 When the acid solution is used as the cleaning fluid, pH of the solution used preferably is adjusted to 4 or less by using hydrochloric acid, a mixed solution of hydrogen peroxide and sulfuric acid and the like. A preferable temperature of the cleaning fluid in that case is 15 to 50°C, and preferable cleaning methods include spray cleaning, ultrasonic cleaning,
35 immersion cleaning and the like. When the solution containing a substance that is capable of forming a complex compound with copper ions is used as the cleaning fluid, an aqueous solution containing 20 to 200 g/liter of

ammonia, monoethanolamine and the like preferably is used. A preferable temperature of the cleaning fluid in that case is 15 to 50°C, and preferable cleaning methods include spray cleaning, ultrasonic cleaning and the like. When the organic solution is used as the cleaning fluid, dipropylene glycol monomethylether and the like preferably are used, and a mixed solution of these organic solutions with water also is preferable. A preferable temperature of the cleaning fluid in that case is 15 to 50°C, and preferable cleaning methods include spray cleaning, ultrasonic cleaning and the like.

The etchant of the present invention is useful especially for producing a printed wiring board with a copper wiring pattern formed by etching. For instance, the etchant is useful when an etching resist is formed on a copper foil, an electroless copper plating film, an electrolytic copper plating film, a sputtered copper film or a multilayer film of them, which are formed on an insulative base material, and copper is etched at a portion that is not covered with the etching resist so as to form a wiring pattern. In this step, a thickness of the etching resist preferably is 40 μm or less. A too-large thickness degrades an etching rate. As the printed wiring board, a rigid board, a flexible board, a metal core board and a ceramic board are available, for example. As the etching resist, a resist including a so-called dry film and a liquid resist, made of resin, and a resist including a single layer of nickel or a plurality of metal layers, e.g., nickel/gold are available, for example.

Furthermore, the etchant of the present invention is useful especially for producing a copper wiring of a substrate on which semiconductor chips are mounted directly, such as a CSP substrate, a TAB substrate and a buildup substrate.

When the etchant of the present invention is used for the above-described wiring pattern producing methods, undercut can be reduced. Therefore, a printed wiring board having a fine and dense wiring pattern can be produced with an improved yield.

Fig. 1 shows cross-sectional views of a method for producing a wiring of a printed wiring board according to one embodiment of the present invention, where Fig. 1A shows a cross section of the printed wiring board prior to etching and Fig. 1B shows a cross section of the same subjected to the etching. In Fig. 1A, reference numeral 1 denotes an electrical insulative member such as a so-called glass epoxy base material in which glass fiber cloth is impregnated with epoxy resin, a so-called phenol paper

base material in which paper is impregnated with phenol resin, a so-called aramid epoxy base material in which aramid fiber non-woven cloth is impregnated with epoxy resin, polyimide film and ceramic base material. Reference numeral 2 denotes a copper layer and 3 denotes an etching resist.

5 As shown in Fig. 1A and Fig. 1B, in the present invention, a portion 2a (See Fig. 1A) of the copper layer 2 on the electrical insulative member 1 that is not covered with the etching resist 3 is etched with the above-described etchant of the present invention so as to form a wiring 4 (See Fig. 1B). In this step, according to the present invention, a difference
10 between a width W_1 of a top portion of the wiring 4 and a width W_2 of a base portion of the wiring 4 (i.e., $(W_2 - W_1)$) can be reduced.
(Examples)

Hereinafter, the present invention will be described more specifically by way of examples. These examples are shown merely for illustrative
15 purpose, and the present invention is not limited to these examples.
(Examples 1 to 9 and Comparative Examples 1 to 3)

Components indicated in Tables 1 and 2 were mixed so as to prepare etchants of Examples 1 to 9 and Comparative Examples 1 to 3. Herein, the etchant of Example 1 had a specific gravity of 1.13 (at 40°C) and an
20 oxidation-reduction potential of 550 mV. Meanwhile, copper foil of 12 μm in thickness was attached to a glass epoxy base material (GEA-67N produced by Hitachi Chemical Co., Ltd.) so as to prepare a copper-clad laminate (base material for printed wiring board) and a dry film resist of 15 μm in thickness (SUNFORT SPG-152 produced by Asahi Chemical Industry
25 Co., Ltd.) was attached thereto, and a wiring pattern with a line and space = 25 $\mu\text{m}/25 \mu\text{m}$ (a width of a line was 25 μm and a space between lines was 25 μm) was formed. Subsequently, the etchants indicated in Tables 1 and 2 were sprayed under the conditions of 40°C and a spraying pressure of 0.15 MPa so as to etch the copper foil, whereby copper wiring patterns were
30 formed. Subsequently, 3wt% of aqueous sodium hydroxide was sprayed thereto so as to peel off the dry film resist.

The thus obtained laminates each were cut and the cross-sectional shape of the formed wiring pattern as shown in Fig. 1 was observed to measure the difference $(W_2 - W_1)$ between the width (W_2) of the base portion
35 of the wiring and the width (W_1) of the top portion. The results are shown in Tables 1 and 2.

(Table 1)

Ex. No.	Composition	W_2-W_1 (μm)
1	cupric chloride 130g/liter hydrochloric acid 50g/liter (as HCl) benzimidazole 8g/liter benzalkonium chloride 0.05g/liter polyethylene glycol 0.01g/liter (average molecular weight 600) ion-exchanged water remainder	4
2	cupric chloride 150g/liter hydrochloric acid 50g/liter (as HCl) benzotriazole 0.4g/liter ethylene glycol monobutyl ether 5g/liter stearyltrimethyl ammonium chloride 0.01g/liter ion-exchanged water remainder	4
3	cupric chloride 150g/liter hydrochloric acid 50g/liter (as HCl) 5-methyl-1H-tetrazole 0.8g/liter benzalkonium chloride 0.002g/liter ion-exchanged water remainder	4.5
4	cupric chloride 300g/liter hydrochloric acid 100g/liter (as HCl) 5-amino-1H-tetrazole 8g/liter 3-methyl-3-methoxybutanol 1g/liter ion-exchanged water remainder	3.5
5	cupric chloride 50g/liter hydrochloric acid 20g/liter (as HCl) benzimidazole 0.3g/liter diethylene glycol 0.01g/liter ion-exchanged water remainder	4
6	cupric chloride 50g/liter hydrochloric acid 150g/liter (as HCl) benzotriazole 0.5g/liter ion-exchanged water remainder	3

(Table 2)

Ex. No.	Composition	W_2-W_1 (μm)
7	cupric chloride 300g/liter hydrochloric acid 20g/liter (as HCl) 5-amino-1H-tetrazole 1.5g/liter 2-phenoxyethanol 1g/liter ion-exchanged water remainder	3
8	cupric chloride 150g/liter hydrochloric acid 50g/liter (as HCl) 5-phenyl-1H-tetrazole 0.3g/liter propylene glycol monomethyl ether 15 g/liter ion-exchanged water remainder	3.5
9	cupric chloride 100g/liter hydrochloric acid 30g/liter (as HCl) 2-methylimidazole 50g/liter diethylene glycol 0.01g/liter ion-exchanged water remainder	4.5
Comp. Ex. 1.	cupric chloride 150g/liter hydrochloric acid 50g/liter (as HCl) 2-aminobenzothiazole 3g/liter ion-exchanged water remainder	12
Comp. Ex. 2	cupric chloride 150g/liter hydrochloric acid 50g/liter (as HCl) 2-aminobenzothiazole 1g/liter polyethylene glycol 5g/liter (average molecular weight 4000) ion-exchanged water remainder	10
Comp. Ex. 3	cupric chloride 150g/liter hydrochloric acid 50g/liter (as HCl) ion-exchanged water remainder	15

As is evident from Tables 1 and 2, the differences (W_2-W_1) between the width (W_2) of the base portion of the wiring and the width (W_1) of the top portion in Examples 1 to 9 were smaller than those in Comparative Examples 1 to 3, and it was confirmed that undercut could be reduced. Thereby, a printed wiring board with a fine and dense wiring pattern can be produced with a high yield.

Herein, in addition to the formation of a wiring on a printed wiring board, the present invention is applicable to various wirings as well, such as a wiring on a glass board, a wiring on a surface of a plastic board and a wiring on a surface of a semiconductor.

CLAIMS:

1. An etchant for copper and copper alloys, comprising an aqueous solution comprising:
5 14 to 155 g/liter of cupric ion source in terms of a concentration of copper ions;
7 to 180 g/liter of hydrochloric acid; and
0.1 to 50 g/liter of azole, the azole comprising nitrogen atoms only as heteroatoms residing in a ring.
10
2. The etchant according to claim 1, wherein 0.1 to 15 g/liter of the azole is present.
3. The etchant according to claim 1, further comprising at least one
15 selected from the group consisting of a cationic surface active agent, glycol and glycol ether.
4. The etchant according to claim 1, wherein 30 to 330 g/liter of cupric chloride is present as the cupric ion source.
20
5. A replenishment solution that is added to the etchant according to claim 1 when the etchant is used repeatedly, the replenishment solution comprising an aqueous solution comprising:
7 to 360 g/liter of hydrochloric acid; and
25 0.1 to 50 g/liter of azole, the azole comprising nitrogen atoms only as heteroatoms residing in a ring.
6. A method for producing a wiring by etching of copper or copper alloys, comprising the step of: etching a portion of a copper layer on an
30 electrical insulative member that is not covered with an etching resist using the etchant according to claim 1 so as to form the wiring.
7. The method for producing a wiring according to claim 6, wherein the etchant is used repeatedly and a replenishment solution is added to the
35 etchant so that a concentration of copper ions in the etchant can be kept at 155 g/liter or less, the replenishment solution comprising an aqueous solution comprising: 7 to 360 g/liter of hydrochloric acid; and 0.1 to 50 g/liter

of azole, the azole comprising nitrogen atoms only as heteroatoms residing in a ring.

8. The method for producing a wiring according to claim 6, wherein
5 after the etching of the copper or the copper alloys using the etchant, the etched portion is washed with a cleaning fluid that is capable of dissolving components of the etchant.

9. The method for producing a wiring according to claim 8, wherein the
10 cleaning fluid is at least one solution selected from the group consisting of an acid solution, a solution containing a substance that is capable of forming a complex compound with copper ions and an organic solution.

10. The method for producing a wiring according to claim 6, wherein the
15 etchant is used repeatedly and the copper or the copper alloys are etched while air is blown into the etchant.