

REPLACED SHEETS

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CHEMICAL ETCHANT FOR PALLADIUM

Field of the Invention

The invention concerns a process for fabrication of devices, in which palladium-containing thin films are either patterned or removed by a chemical etching procedure.

Background of the Invention

In the fabrication of many electronic devices, palladium (and its alloys) is often used as a substitute for gold, e.g., as a layer plated on top of copper or nickel, and may be provided with a flash of gold, such as hard gold. It is used as a surface for plating gold, copper, nickel and various other metals thereon or to preclude diffusion of one metal into another metal, for example nickel into gold. Due to the cost of precious metals it has become extremely important that means be provided for stripping them from the underlaying metals completely and with minimum contamination and corrosion, both to remove imperfectly formed deposits and to permit recovery of the metal from discarded or worn-out parts.

Numerous means for effecting the removal of precious metals from substrates may be found in the prior art. Unfortunately, while the prior art processes are effective in removing gold, the prior art processes are quite ineffective for palladium.

As an exception to this generalization Augustus Fletcher et al. disclose in U.S. Patent No. 4,548,791 a thallium-containing composition for effectively stripping palladium. The solution contains a thallium compound in addition to a nitrobenzoate derivative, a soluble cyanide and certain optional ingredients, including lead compounds. However, while this solution effectively removes gold and palladium, it actively attacks copper and copper-containing substrates, rendering this solution unsuitable for use in those instances when palladium forms one of the films or layers of a composite including copper or is on a copper-containing substrate. An example of the latter would be a palladium film on a copper-based lead frame or on copper based connections, etc.

Thus, the need remains for a composition which is capable of stripping deposits comprising palladium and other precious metals, such as gold flash-coated palladium layers, without an undue damage to an underlaying metal, such as copper.

Summary of the Invention

A cyanide based aqueous solution for stripping palladium from copper-containing substrate. The solution includes a cyanide radical source compound, Na_2CO_3 , a nitrobenzoic acid, NaOH , thallium compound, an organo mercapto

compound, and water. The presence of the organo mercapto compound in thallium containing cyanide bath permits efficient stripping of palladium from copper containing substrates with minimum corrosion damage to the substrate.

Brief Description of the Drawings

- 5 FIG. 1 is a chart of plots representing the effect of varied amounts in grams per liter (g/l) of 2-mercaptobenzothiazole on the etching rate of Pd and Cu and a plot of Pd/Cu etching rate ratio.

Detailed Description

- 10 The etching solution embodying the invention is a three-part composition including an oxidant, an inhibitor and a salt mixture. The three parts are prepared separately and are mixed shortly before the use.

- The oxidant is prepared as Concentrate I by combining 15-40 gram per liter (g/l) sodium hydroxide (NaOH), 60-120 g/l 3-nitrobenzoic acid ($O_2N \cdot C_6H_4 \cdot CO_2H$), 0.3-0.6 g/l thallous nitrate ($TlNO_3$) and sufficient water to
15 prepare one liter of Concentrate I.

 The inhibitor is prepared as Concentrate II by dissolving 10 - 40 g of 2-mercaptobenzothiazole in a mixture of methylethyl ketone (MEK) and isopropanol (IPA) mixed in a ratio of 7:3 and in an amount sufficient to prepare 1 liter of Concentrate II.

- 20 The salt mixture is prepared by mixing potassium cyanide (KCN), sodium carbonate (Na_2CO_3) and water so as to prepare one liter of salt mixture solution containing 50-200 g/l of KCN and 25-100 g/l Na_2CO_3 . Instead of KCN, 40-160 g/l sodium cyanide (NaCN) may be used in the salt mixture.

- The stripping solution is prepared by adding in small portions
25 Concentrate I and Concentrate II, in succession, to the salt mixture solution, mixing thoroughly after each addition and then adding D.I. water in an amount sufficient to provide one liter of solution containing

- 50-200 g/l KCN or 40-160 g/l NaCN
 25-100 g/l Na_2CO_3
30 100-400 ml/l Concentrate I, and
 4-20 ml/l Concentrate II

 The so produced stripping solution shall
comprise the following ingredients:

- 50-200 g/l KCN or 40-160 g/l NaCN
35 25-100 g/l Na_2CO_3

10-50 g/l 3-nitrobenzoic acid
4-10 g/l NaOH
0.075-0.15 g/l TlNO_3
0.1-0.5 g/l 2-mercaptobenzothiazole

- 5 The pH of the stripping solution may range from 10 to 14, preferably from 10.5 to 12.5.

In preparing the three parts of the stripping solution, other compounds may be used instead of or in combination with a preferred compound being used. For example, instead of or in addition to the 3-nitrobenzoic acid, acids and their
10 derivatives selected from 2-nitrobenzoic acid, 4-nitrobenzoic acid, 2-nitrobenzenesulfonic acid, 3-nitrobenzenesulfonic acid, 4-nitrobenzenesulfonic acid, chloronitrobenzoic acid isomers, chloronitrobenzenesulfonic acid isomers, and mixtures of the above acids and their derivatives, may be used as such or in the form of their alkali salts. The thallium salts may be selected from the group consisting of
15 thallos (Tl^+) or thallic (Tl^{3+}) salts of nitric, sulfuric, phosphoric, and acetic acids, and other soluble thallium salts. The inhibitor may be prepared using, instead of or in addition to 2-mercaptobenzothiazole, the following compounds:
2-mercaptobenzoxazole, 2-benzimidazolethiol, 2-mercapto-5-methylbenzimidazole and their derivatives. These inhibitors have been mentioned by E. H. Too et al. in
20 U.S. Patent 4,483,739 issued November 20, 1984 as a corrosion inhibitor in gold stripping solutions. However, only the 2-mercaptobenzothiazole exhibited the synergistic effect in a thallium containing solution.

An exemplary stripping solution is prepared as described in Examples 1 - 4 below.

25 - Example 1

To prepare 1 liter of Concentrate I dissolve 30g of solid sodium hydroxide (NaOH) in 850 ml of D.I. water, dissolve 120 g solid 3-nitrobenzoic acid ($\text{O}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$) adding it in portions to the NaOH solution, prepare an aqueous solution containing 25 g/l of Tl by dissolving 32.6 g of thallos nitrate
30 (TlNO_3) per liter and add 16 ml of this solution to the NaOH and nitrobenzoic acid solution, add sufficient D.I. water to make one liter of solution, and mix thoroughly.

Example 2

- To prepare 1 liter of Concentrate II prepare a mixed solvent by combining 7 volume units of methylethyl ketone (MEK) and 3 volume units of isopropanol (IPA), dissolve 30 g 2-mercaptobenzothiazole in 950 ml of the mixed solvent, and, after filtering the solution, fill the filtrate with the mixed solvent to make one liter of
- 5 Concentrate II.

Example 3

To prepare one liter of salt mixture solution dissolve 167 g KCN and 83 g Na_2CO_3 in one liter of D.I. water.

Example 4

- 10 To prepare one liter of the exemplary stripping solution add 250 ml of Concentrate I of Example 1 in small portions to 600 ml of salt mixture solution of Example 3, add 10 ml of Concentrate II of Example 2, mix thoroughly, and fill with sufficient D.I. water to make one liter of stripping solution. The resultant exemplary stripping solution will have the following composition:
- 15 100 g/l potassium cyanide (KCN),
50 g/l sodium carbonate (Na_2CO_3),
30 g/l 3-nitrobenzoic acid ($\text{O}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$),
7.5 g/l sodium hydroxide NaOH,
0.1 g/l thallium as thallos nitrate (0.13 g/l TlNO_3), and
20 0.3 g/l 2-mercaptobenzothiazole ($\text{C}_7\text{H}_5\text{NS}_2$).

The salt mixture solution and Concentrates I and II are preferably combined and heated to a temperature within a range of from 40 to 45°C shortly before use. The stripping is conducted at this temperature with moderate to high agitation.

- 25 Experiments were conducted by immersing a Cu foil Pd-plated on both sides and an unplated Cu foil in separate vessels containing the same solution in each experiment. The solution was kept at a temperature ranging from 40 to 45°C and with moderate to high agitation. The experiments show that presence of both thallium and 2-mercaptobenzothiazole in a cyanide etching solution (Examples 5, 8,
- 30 11 and 13) leads to an increase in the etching rate of Pd and decrease in the etching rate of Cu relative to experiments in which the etching solution contained neither thallium nor 2-mercaptobenzothiazole (Examples 6 and 9) or contained only thallium (Example 10) or only 2-mercaptobenzothiazole (Examples 7 and 12).

The experiments show that while addition of thallium (Example 10) to a cyanide etching solution (Examples 6 and 9) leads to an increase in the rate of removal of Pd while the rate of Cu etching remains high, addition of 2-mercaptobenzothiazole (Examples 7 and 12) to the cyanide etching solution reduces the etching rate of Pd but has hardly any effect on the etching rate of Cu in the same solution. It is only when both the thallium and the 2-mercaptobenzothiazole were included in the cyanide-etching solution, that an unexpected, synergistic effect took place, namely, removal of Pd was increased while removal of Cu decreased drastically. Copper corrosion is inhibited only when both additives are present, that is 2-mercaptobenzothiazole is so effective only in the presence of thallium in the solution. This is in spite of the fact that Tl^+ ion forms a precipitate with 2-mercaptobenzothiazole, whereby the concentrations of both species in the aqueous solution are diminished.

Below are the experiments that show the effect of thallium ion and 2-mercaptobenzothiazole on stripping Pd from Cu substrate and on Cu corrosion.

Example 5

A Pd stripping solution of Example 4, that is one containing both Tl and 2-mercaptobenzothiazole, was used to remove Pd from a Cu substrate. A Cu foil electroplated with Pd on both sides was immersed in this solution at 42°C with moderate agitation for one minute. During this interval 1.0 micrometer per minute ($\mu\text{m}/\text{min}$) of Pd thickness was removed from the surface. An unplated Cu foil immersed in this solution under the same conditions lost 0.32 $\mu\text{m}/\text{min}$.

Example 6

A Pd stripping solution similar to that of Example 4, but containing neither Tl nor 2-mercaptobenzothiazole, was used to compare the etching rate of this solution with that of Example 5. When immersed in the solution under the same conditions, Pd was stripped from the Pd-plated Cu-foil at a rate of 0.37 $\mu\text{m}/\text{min}$ and Cu from the unplated Cu foil at a rate of 4.3 $\mu\text{m}/\text{min}$ conditions.

Example 7

After the addition of 1 g/l of 2-mercaptobenzothiazole to the stripping solution of Example 6, the Pd stripping rate was reduced to 0.08 $\mu\text{m}/\text{min}$, but the Cu stripping

rate was at 4.4 $\mu\text{m}/\text{min}$.

Example 8

After the addition of 300 ppm thallium to the stripping solution of Example 7 which already contained 1 g/l of 2-mercaptobenzothiazole, the Pd stripping rate was
5 increased to 1.0 $\mu\text{m}/\text{min}$; however a copper foil immersed under the same conditions lost only 0.32 $\mu\text{m}/\text{min}$ in thickness. Due to the large concentration of 2-mercaptobenzothiazole, relative to the recommended 0.1-0.5 g/l range, much of the added thallium was precipitated, and the potential effect of thallium addition was not fully realized.

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Example 9

A Pd stripping solution containing 100 g/l potassium cyanide (KCN), 50 g/l sodium carbonate (Na_2CO_3), 7.5 g/l sodium hydroxide (NaOH), and 30 g/l 4-nitrobenzoic acid ($\text{O}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$), was prepared without either thallium or 2-mercaptobenzothiazole. A copper foil electroplated with palladium on both sides
15 and an unplated Cu foil were immersed in separate vessels in this solution at 42°C with moderate agitation, for one minute. During this interval, 0.30 μm (average) of palladium thickness were dissolved from the surface. A copper foil immersed under the same conditions lost 5.1 μm (average) thickness of copper metal.

Example 10

20 100 ppm thallium (as TlNO_3) were added to the solution of Example 9. A palladium-plated copper foil was immersed under the same conditions as in Example 9. This time, 0.97 μm (average) of palladium were stripped. An unplated copper foil immersed under the same conditions lost 5.3 μm (average) of thickness. It can be seen that through the addition of thallium the attack on palladium was
25 accelerated, while the rate of attack on copper remained high.

Example 11

300 ppm 2-mercaptobenzothiazole were added to the solution of Example 10, which already contained 100 ppm thallium. A small amount of precipitate formed, which was not removed. A palladium-plated copper foil, immersed under the same \n
30 conditions as in Example 9, lost 0.88 $\mu\text{m}/\text{min}$ (average) of Pd thickness; but in

contrast to Examples 9 and 10, an unplated copper foil lost only 0.18 $\mu\text{m}/\text{min}$ (average) under the same conditions.

Example 12

300 ppm 2-mercaptobenzothiazole were added to a fresh solution according to
5 Example 9. The attack rate on palladium on a palladium plated copper foil immersed under the same conditions as in Example 9 was reduced to 0.18 $\mu\text{m}/\text{min}$ (average); the attack rate on copper remained high, being only reduced to 4.8 $\mu\text{m}/\text{min}$ (average). This shows that in the absence of thallium the addition of 2-mercaptobenzothiazole to a conventional stripping solution does not significantly
10 inhibit the rate of copper corrosion.

Example 13

100 ppm thallium were added to the solution of Example 12. A small amount of precipitate formed which was not removed. Under the same conditions as in Example 9, 0.77 $\mu\text{m}/\text{min}$ (average) of palladium were stripped from a palladium
15 plated copper foil, but only 0.047 $\mu\text{m}/\text{min}$ (average) were lost from an unplated copper foil. This result and the results of Examples 5, 8 and 11 prove the synergistic inhibiting effect on copper corrosion of the proposed combination of thallium and 2-mercaptobenzothiazole in this type of stripping solution.

Another experiment shows the influence of 2-mercaptobenzothiazole
20 added in increments to a thallium-containing stripping solution.

Example 14

Incremental amounts of 2-mercaptobenzothiazole (2-MBT) were added to a stripping solution containing 100 g/l potassium cyanide (KCN), 50 g/l sodium carbonate (Na_2CO_3), 7.5 g/l sodium hydroxide (NaOH), 30 g/l 3-nitrobenzoic acid
25 ($\text{O}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$) and 100 ppm of thallium. The following stripping rates were observed on a Pd-plated Cu foil and on an unplated Cu foil when immersed in the stripping solution at 45°C with moderate agitation:

2-MBT Content, g/l	Pd Stripping Rate, $\mu\text{m}/\text{min}$	Cu Stripping Rate, $\mu\text{m}/\text{min}$
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	0.0	1.51	2.67
	0.1	0.82	0.21
	0.25	0.58	0.024
	0.5	0.48	0.012
5	1.0	0.34	0.006

These data show that the copper corrosion is much more inhibited than the palladium corrosion by increasing addition of 2-mercaptobenzothiazole. The plot shown in FIG. 1 of the drawing, presents the above data as curve 1 (□) representing the Pd stripping rate and curve 2 (◇) representing the Cu stripping rate, both in $\mu\text{m}/\text{min}$.
 10 Curve 3 (•) represents a derived ratio of Pd stripping rate versus Cu stripping rate (Pd-rate/Cu-rate).

The high level of copper passivation obtained with 2-mercaptobenzothiazole in the TI-containing stripper solution is surprising. Other additives typically in commercial use for the protection of copper in nickel-stripping
 15 were found virtually ineffective in this palladium stripping solution. For example, benzotriazole slowed down the corrosion rate of copper to only one half ($1.8 \mu\text{m}/\text{min}$ vs $3.8 \mu\text{m}/\text{min}$ without inhibitor); thiourea did not inhibit the corrosion of copper at all and accelerated the attack on nickel by a factor of 10. By contrast, 2-mercaptobenzothiazole decreased the rate of attack on copper by a factor of 50-
 20 250.

Additional advantages and modifications will readily occur to those skilled in the art. Therefore, the invention in its broader aspects is not limited to the specific details, representative devices, and illustrated examples shown and described. Accordingly, various modifications may be made without departing from
 25 the spirit or scope of the general inventive concept as defined by the appended claims and their equivalents.



Claims:

1. A method for stripping palladium and its alloys from copper-containing substrates, which comprises
preparing a palladium stripping solution and immersing parts to be
5 stripped of Pd into said solution, in which said stripping solution is prepared by
preparing an oxidant solution comprising a hydroxide, nitrobenzoic acid
and thallium compound in water,
preparing a Cu-corrosion inhibitor solution comprising an organo
mercapto compound in solvent therefore,
10 preparing a salt solution comprising cyanide radical source compound
and Na_2CO_3 in water, and
mixing the three solutions by adding oxidant solution in increments and
the inhibitor solution to the salt solution under mixing.
2. A method of preparing an aqueous stripping solution for stripping
15 palladium from copper-containing substrates, which comprises
preparing an oxidant solution comprising a hydroxide, a nitrobenzoic
acid thallium compound in water,
preparing a Cu-corrosion inhibitor solution comprising an organo
mercapto compound in solvent therefore,
20 preparing a salt solution comprising cyanide radical source compound
and Na_2CO_3 in water, and
mixing the three solutions by adding oxidant solution in small portions
and the inhibitor solution to the salt solution under mixing.
3. A solution for stripping palladium and its alloys from copper-
25 containing substrates, which is comprised of from 50 to 200 parts of a cyanide
radical source compound, 25-100 parts of Na_2CO_3 , from 10 to 50 parts of a
nitrobenzoic acid, from 4-10 parts of NaOH, from 0.075 to 0.15 parts of a thallium
compound, from 0.1 to 0.5 parts of an organo mercapto compound, and water to
make up one liter of solution said parts being expressed on a gram per liter (g/l)
30 basis.
4. The method of claim 1 or 2, or the solution of claim 3, in which the so
prepared stripping solution comprises





- 50-200 g/l KCN or 40-100 g/l NaCN, (for example 100g/l KCN)
25-100 g/l Na_2CO_3 , (for example 50g/l)
10-50 g/l 2-, 3- or 4-nitrobenzoic acid (for example 30g/l 2,3 or 4
nitrobenzoic acid)
- 5 4-10 g/l NaOH, (for example 7.5g/l NaOH)
 0.075-0.15 g/l TlNO_3 , (for example 0.1g/l thallium or thallos nitrate
(0.13g/l TlNO_3)
 0.1-0.5 g/l 2-mercaptobenzothiazole, (for example 0.3 g/l 2-
mercaptobenzothiazole).
- 10 5. The method of claim 1 or 2, or the solution of claim 3, in which
 a) said oxidant solution is prepared by
 dissolving 30g of solid sodium hydroxide in 850 ml of D.I. water,
 dissolving 120 g of solid nitrobenzoic acid, selected from 2-, 3- and 4-
nitrobenzoic acids, while adding it in portions to the sodium hydroxide solution,
15 preparing an aqueous solution containing 25 g/l of Tl by dissolving 32.6
 g of thallos nitrate (TlNO_3) per liter and adding 16 ml of this solution to the NaOH
 and nitrobenzoic acid solution, and
 adding sufficient D.I. water to make one liter of oxidant solution;
 b) said inhibitor solution is prepared by
20 combining 7 volume units of methylethyl ketone and 3 volume units of
 isopropanol,
 dissolving 30 g of 2-mercaptobenzothiazole in 950 ml of the mixed
 solvent, and
 after filtering this solution, filling the filtrate with the mixed solvent to
25 make one liter of the inhibitor solution;
 c) said salt solution is prepared by dissolving 167 g KCN and 83 g
 Na_2CO_3 in one liter of water; and
 d) preparing one liter of stripping solution by
 adding 250 ml of the oxidant solution in increments to 600 ml of the salt
30 solution,
 adding 10 ml of the inhibitor solution,
 mixing the combination thoroughly, and
 filling with sufficient D.I. water to make one liter of the stripping
 solution.





6. The method of claim 1 or 2, in which the prepared stripping solution is heated to a temperature ranging from 40 to 45°C, and said stripping is being conducted under moderate agitation.

7. The method of claim 1 or 2, in which said oxidant solution, said
5 inhibitor solution and said salt mixture solution are combined only prior to the use of the stripping solution, or

in which said oxidant solution is added in increments to said salt mixture solution, followed by the addition of the inhibitor solution and addition of D.I. water, and mixing of the components.

10 8. The method of claim 1 or 2, or the solution of claim 3, in which said organo mercapto compound is selected from the group consisting of 2-mercaptobenzothiazole, 2-mercaptobenzoxazole, 2-benzimidazolethiol, 2-mercapto-5 methylbenzimidazole, their derivatives and their mixtures.

15 9. The method of claim 1 or 2, or the solution of claim 3, in which said organo mercapto compound comprises 2-mercaptobenzothiazole.

10. The method of claim 1 or 2, or the solution of claim 3, in which said cyanide radical compound comprises at least one of KCN and NaCN.

11. The method of claim 1 or 2, or the solution of claim 3, in which said nitrobenzoic acid derivative is selected from the group consisting of 2-nitrobenzoic
20 acid, 3-nitrobenzoic acid, 4-nitrobenzoic acid, 2-nitrobenzenesulfonic acid, 3-nitrobenzenesulfonic acid, 4-nitrobenzenesulfonic acid, chloronitrobenzoic acid isomers, chloronitrobenzenesulfonic acid isomers, and mixtures of these acids and their derivatives.

12. The method of claim 1 or 2, or the solution of claim 3, in which said
25 nitrobenzoic acid derivative comprises at least one of 2-nitrobenzoic acid, 3-nitrobenzoic acid and 4-nitrobenzoic acid.

13. The method of claim 1 or 2, or the solution of claim 3, in which said thallium compound is selected from the group consisting of thalious (Tl^+) and thallic (Tl^{3+}) salts of nitric, sulfuric, phosphoric and acetic acids, and other soluble thallium





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salts, and/or in which the thallium compound comprises a nitrate.

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