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(54) ELECTROLESS PALLADIUM PLATING BATH

(57) A plating bath at least contains a palladium compound, a reducing agent, a complexing agent, and a stabilizer. The stabilizer is an organic compound in which a divalent sulfur compound is bonded to a compound with a heterocyclic structure, and the organic compound contains neither a thiol group nor a disulfide bond.

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Description

BACKGROUND

[0001] The present disclosure relates to an electroless palladium plating bath.

[0002] In the field of electronic industry, for example, an electroless nickel (Ni)/electroless palladium (Pd)/immersion gold (Au) (ENEPIG) has been used as a surface treatment for mounts or terminals of printed circuit boards or IC packages. Using this ENEPIG process, a plating film sequentially including an electroless nickel plating film, an electroless palladium plating film, and an immersion gold plating film is obtained.

[0003] The palladium film exhibits a good electrical conductivity and a high corrosion resistance, and moreover has the function of avoiding the diffusion of underlying nickel onto the gold surface due to thermal history. Thus, the palladium film plays an important role in the ENEPIG process described above.

[0004] In general, the plating bath is required to be highly stable. In a typical electroless palladium plating bath, an ethylenediaminetetraacetic acid or a salt thereof, for example, is used as a stabilizer. However, the plating bath is easily biodegradable and is therefore not sufficiently stable.

[0005] To address the problem, an electroless palladium plating bath having an organic compound containing divalent sulfur blended therein has been proposed. It is described (see, e.g., Japanese Patent No. 3972158) that the stability of a plating bath improves by using an organic compound containing divalent sulfur.

SUMMARY

[0006] Here, the typical plating bath described above has improved stability by blending the organic compound containing divalent sulfur, but has a problem of lower deposition properties of palladium onto a nickel plating film.

[0007] There are devices that address the problem by using nickel plating films containing phosphorus (P) (nickel plating films having a concentration of phosphorus in the film ranging from 4% to 8%). In recent years, however, with an increase in the guaranteed operating temperatures of the devices, there is an increasing demand for a nickel plating film with a lower phosphorus content (a nickel plating film having a concentration of phosphorus in the film being less than 4%) that is applicable to a device with a high guaranteed operating temperature. The typical plating bath described above has the problem in particular that the deposition properties of palladium onto a nickel plating film having a lower phosphorus content is reduced significantly. Development of an electroless palladium plating bath applicable to nickel plating films having a lower phosphorus content is therefore desired.

[0008] In view of the above problems, it is an objective of the present disclosure to provide an electroless palladium plating bath enabling improvement in stability of a plating bath, while reducing the deterioration in the deposition properties of palladium onto a nickel plating film.

[0009] In order to achieve the above objective, an electroless palladium plating bath according to the present disclosure at least contains: a palladium compound; a reducing agent; a complexing agent; and a stabilizer. The stabilizer is an organic compound in which a divalent sulfur compound is bonded to a compound with a heterocyclic structure, and the organic compounds contains neither a thiol group nor a disulfide bond.

[0010] The present disclosure provides a plating bath with improved stability, while reducing the deterioration in the deposition properties of palladium onto a nickel plating film.

DETAILED DESCRIPTION

[0011] Now, an electroless palladium plating bath according to the present disclosure will be described.

<Electroless Palladium Plating Bath>

[0012] The electroless palladium plating bath according to the present disclosure contains a palladium compound, a reducing agent, a complexing agent, and a stabilizer.

(Palladium Compound)

[0013] The palladium compound is a palladium ion source for palladium plating. The palladium compound may be at least water soluble. Examples of the palladium compound include: water-soluble inorganic palladium salts such as palladium chloride, palladium sulfate, and palladium acetate; and water-soluble organic palladium salts such as tetraamminepalladium hydrochloride, tetraamminepalladium sulfate, tetraamminepalladium acetate, tetraamminepalladium nitrate, and bis(ethylenediamine)palladium(II)chloride. Note that these palladium compounds may be used alone or two or more kinds may be used in a mixture.

[0014] The concentration of the palladium ions in the electroless palladium plating bath is not particularly limited. However, a too low concentration of the palladium ions may significantly lower the rate of deposition of the plating film. The concentration is thus preferably 0.1 g/L or more, more preferably 0.3 g/L or more, and still more preferably 0.5 g/L or more. On the other hand, a too high concentration of the palladium ions may cause abnormal deposition which deteriorates the physical properties of the film. The concentration is thus preferably 10 g/L or less, more preferably 5 g/L or less, and still more preferably 3 g/L or less.

[0015] The concentration of the palladium ions can be measured by atomic absorption spectrometry (AAS) using an atomic absorption spectrophotometer.

(Reducing Agent)

[0016] The reducing agent has the function of depositing palladium in an electroless palladium plating bath. As the reducing agent, various known kinds of reducing agent can be used. Examples of the reducing agent include formic acid and salts thereof, hydrazines, hypophosphorous acid and salts thereof, phosphorous acid and salts thereof, amine borane compounds, hydroboration compounds, formalin, and ascorbic acid and salts thereof.

[0017] Examples of the above mentioned salts include: alkali metal salts such as potassium and sodium salts; alkaline earth metal salts such as magnesium and calcium salts; ammonium salts; quaternary ammonium salts; and amine salts containing primary to tertiary amines.

[0018] Examples of the amine borane compounds include dimethylamine borane (DMAB) and trimethylamine borane (TMAB). Examples of the hydroboration compounds include alkali metal borohydride salts such as sodium borohydride (SBH) and potassium borohydride (KBH).

[0019] Among these reducing agents, formic acid or a salt thereof (e.g., sodium formate) is used in one preferred embodiment in view of achieving both the stability of the plating bath and the deposition properties of the plating film. These reducing agents may be used alone or two or more kinds may be used in a mixture.

[0020] The content of the reducing agent in the electroless palladium plating bath (i.e., the single amount where the agent is used alone, and the total amount where two or more kinds are used in a mixture) may be adjusted as appropriate in consideration of the rate of deposition in the plating processing and the stability of the plating bath. The lower limit is preferably 1 g/L or more, more preferably 3 g/L or more, still more preferably 5 g/L or more, and particularly preferably 10 g/L or more. The upper limit of the content of the reducing agent is preferably 100 g/L or less, more preferably 80 g/L or less, and still more preferably 50 g/L or less.

(Complexing Agent)

[0021] The complexing agent has the main function of stabilizing the solubility of palladium in the electroless palladium plating bath. As the complexing agent, various known kinds of complexing agent can be used. Examples of the complexing agent include at least one selected from the group consisting of ammonia and amine compounds, among which an amine compound is selected in a more preferred embodiment. Examples of the amine compounds include methylamine, dimethylamine, trimethylamine, benzylamine, methylenediamine, ethylenediamine, ethylenediamine derivatives, tetramethylenediamine, diethylenetriamine, ethylenediaminetetraacetic acid (EDTA) or alkali metal salts thereof, EDTA derivatives, and glycine. These complexing agents may be used alone or two or more kinds may be used in a mixture.

[0022] The content of the complexing agent in the electroless palladium plating bath (i.e., the single amount where the agent is used alone, and the total amount where two or more types are used in a mixture) may be adjusted as appropriate in consideration of the stable solubility of palladium. The lower limit is preferably 0.1 g/L or more, more preferably 1 g/L or more, and still more preferably 3 g/L or more. The upper limit of the content of the complexing agent is preferably 15 g/L or less and more preferably 10 g/L or less.

(Stabilizer)

[0023] The stabilizer is added for the purpose of stabilizing the plating bath, improving appearance after the plating, adjusting the rate of forming a plating film, and other purposes. In the electroless palladium plating bath according to the present disclosure, an organic compound represented by the following Formula (1) can be used in which a divalent sulfur compound (i.e., a compound containing divalent sulfur) is bonded to a compound with a heterocyclic structure.
[Chemical 1]

$$R_1\text{-}R_2... \qquad (1)$$

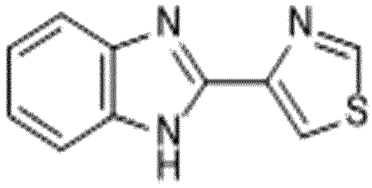
where R_1 is the compound with the heterocyclic structure, and R_2 is the divalent sulfur compound. R_1-R_2 represents an organic compound with neither a thiol group nor a disulfide bond.

[0024] Examples of the compound R_1 with a heterocyclic structure include compounds with a nitrogen-containing heterocyclic structure or a sulfur-containing heterocyclic structure such as imidazole, imidazolidine, imidazoline, oxadiazole, oxazine, thiadiazole, thiazole, thiazolidine, tetrazole, triazine, triazole, piperazine, piperidine, pyrazine, pyrazole, pyrazolidine, pyridine, pyridazine, pyrimidine, pyrrole, pyrrolidine, benzothiazole, benzimidazole, isoquinoline, thiophene, tetrahydrothiophene, pentamethylene sulfide, and derivatives thereof.

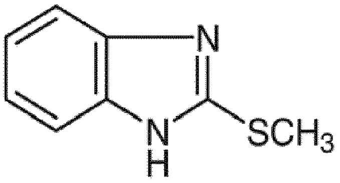
[0025] Examples of the divalent sulfur compound R_2 include thiadiazole, thiazole, thiazolidine, benzothiazole, thiophene, tetrahydrothiophene, methanethiol, benzenethiol, pentamethylene sulfide, dimethyl sulfide, methyl mercaptan, ethyl mercaptan, allyl mercaptan, thiopropionic acid, thioacetic acid, ethyl methyl sulfide, 1-propanethiol, 2-propanethiol, 2-aminoethanethiol, 2-mercaptoethanol, 4-mercaptopyridine, dimethyl sulfoxide, S-methyl thioacetate, ethyl sulfide, methylpropyl sulfide, 1-butanethiol, thioglycolic acid, 2-(methylthio)ethanol, 3-mercapto-1-propanol, 2-methylthiazoline, cyclopentanethiol, 2-methyltetrahydrothiophene, pentamethylene sulfide, thiomorpholine, S-methyl thiopropionate, 3-mercaptopropionic acid, and derivatives thereof.

[0026] Examples of the stabilizer represented by Formula (1) include 2-(4-thiazolyl)benzimidazole, 2-(methylthio)benzimidazole, 2-(methylthio)benzothiazole, (2-benzothiazolylthio)acetic acid, 3-(2-benzothiazolylthio)propionic acid, 2-(methylthio)pyridine, (4-pyridylthio)acetic acid, 4,4'-dipyridyl sulfide, 2-methylthio-4-pyrimidinol, S-methylthiobarbituric acid, 4-amino-6-chloro-2-(methylthio)pyrimidine, 5-(methylthio)-1H-tetrazole, 5-(ethylthio)-1H-tetrazole, N-(phenylthio)phthalimide, and 5-(methylthio)thiophene-2-carboxaldehyde. Note that these stabilizers may be used alone or two or more kinds may be used in a mixture. Chemical formulas of these stabilizers are as follows.

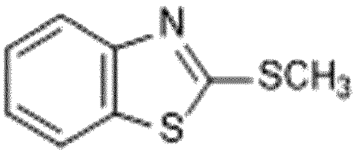
[Chemical 2]



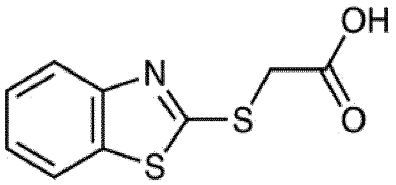
2-(4-thiazolyl)benzimidazole



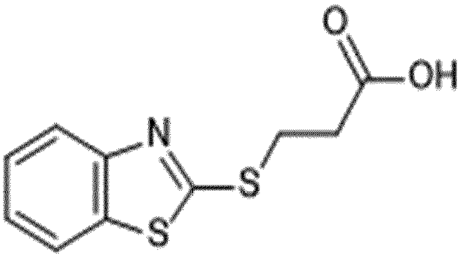
2-(methylthio)benzimidazole



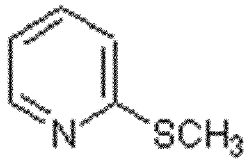
2-(methylthio)benzothiazole



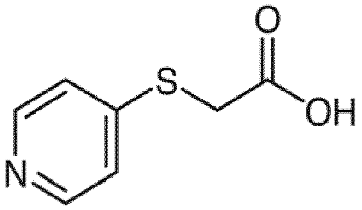
(2-benzothiazolylthio)acetic acid



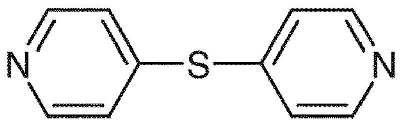
3-(2-benzothiazolylthio)propionic acid



2-(methylthio)pyridine

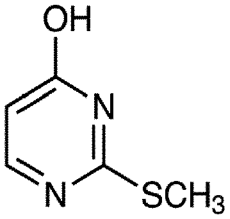


(4-pyridylthio)acetic acid

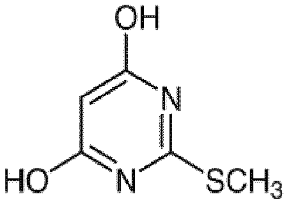


4,4′ -dipyridyl sulfide

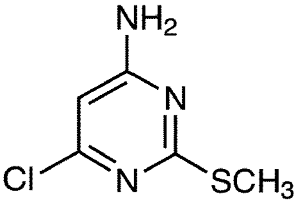
[Chemical 3]



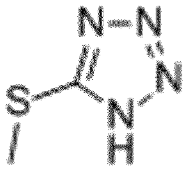
2-methylthio-4-pyrimidinol



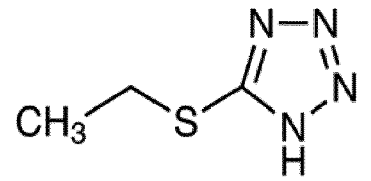
S-methylthiobarbituric acid



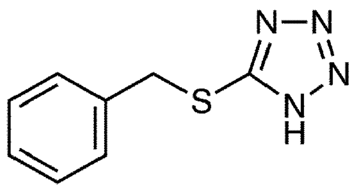
4-amino-6-chloro-2-(methylthio)pyrimidine



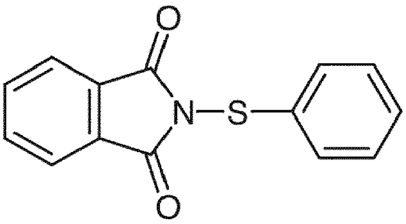
5-(methylthio)-1H-tetrazole



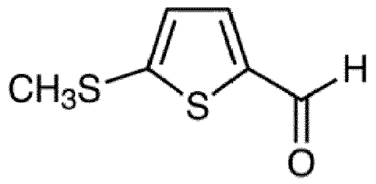
5-(ethylthio)-1H-tetrazole



5-(benzylthio)-1H-tetrazole



N-(phenylthio)phthalimide



5-(methylthio)thiophene-2-carboxaldehyde

[0027] The organic compound (R_1-R_2) used as the stabilizer in the electroless palladium plating bath according to the present disclosure includes an organic compound in which the divalent sulfur compound R_2 bonded to the compound R_1 with the heterocyclic structure derives from a thiol (-SH) group-containing compound.

[0028] More specifically, for example, the 2-(methylthio)benzimidazole is an organic compound (R_1-R_2) in which benzimidazole as R_1 and methanethiol as R_2 are bonded. The compound contains no thiol (-SH) group in the state of R_1-R_2 as shown in the chemical formula. However, since R_2 (i.e., methanethiol) before being bonded to R_1 contains the thiol (-SH) group, R_2 bonded to R_1 derives from the compound (i.e., methanethiol) containing the thiol (-SH) group. The same applies to 2-(methylthio)benzothiazole (where R_1 is benzothiazole and R_2 is methanethiol) and 2-(methylthio)pyridine, (where R_1 is pyridine and R_2 is methanethiol).

[0029] For example, (2-benzothiazolylthio)acetic acid contains no thiol (-SH) group in the state of R_1-R_2 (where R_1 is benzothiazole and R_2 is thioacetic acid) as shown in the chemical formula. However, since R_2 (i.e., thioacetic acid) before being bonded to R_1 contains the thiol (-SH) group, R_2 bonded to R_1 derives from the compound (i.e., thioacetic acid) containing the thiol (-SH) group. The same applies to (4-pyridylthio)acetic acid (where R_1 is pyridine and R_2 is thioacetic acid).

[0030] For example, 3-(2-benzothiazolylthio)propionic acid contains no thiol (-SH) group in the state of R_1-R_2 (where R_1 is benzothiazole and R_2 is thiopropionic acid) as shown in the chemical formula. However, since R_2 (i.e., thiopropionic acid) before being bonded to R_1 contains the thiol (-SH) group, R_2 bonded to R_1 derives from the compound (i.e., thiopropionic acid) containing the thiol (-SH) group.

[0031] For example, 4,4'-dipyridyl sulfide contains no thiol (-SH) in the state of R_1-R_2 (where R_1 is pyridine and R_2 is 4-mercaptopyridine) as shown in the chemical formula. However, since R_2 (i.e., 4-mercaptopyridine) before being bonded to R_1 contains the thiol (-SH) group, R_2 bonded to R_1 derives from the compound (i.e., 4-mercaptopyridine) containing the thiol (-SH) group.

[0032] Here, as described above, the plating bath has improved stability by blending the organic compound containing divalent sulfur, but has the problem of lower deposition properties of palladium onto the nickel plating film. In particular, there is a problem of significantly lower deposition properties of palladium onto a nickel plating film having a low phosphorus content.

[0033] The present inventors have studied the above problem and found the following: Using a stabilizer made of an organic compound in which a divalent sulfur compound is bonded to a compound with a heterocyclic structure (i. e., R_1-R_2 described above) reduces a reduction in the deposition properties of palladium on the nickel plating film and improves the stability of the plating bath.

[0034] The present inventors also have found the following: Using an organic compound having a thiol group or a disulfide bond, among organic compounds in which a divalent sulfur compound is bonded to a compound with a heterocyclic structure, alters the thiol group or the disulfide bond due to an oxidation-reduction reaction in the plating bath (i.e., a disulfide bond is generated by an oxidation reaction of the thiol group, and a thiol group is generated by a reduction reaction of the disulfide bond), which changes the deposition properties of palladium and reduces the stability of the plating bath.

[0035] That is, it is possible to achieve both of the deposition properties of palladium and the stability of the plating bath by using, as the stabilizer, an organic compound in which a divalent sulfur compound is bonded to a compound with a heterocyclic structure and which contains neither a thiol group nor a disulfide bond.

[0036] It is also possible to deposit palladium even on a tiny region on the nickel plating film with a low phosphorus content.

[0037] The content of the stabilizer in the electroless palladium plating bath (i.e., the single amount where the agent is used alone, and the total amount where two or more kinds are used in a mixture) may be adjusted as appropriate in consideration of the deposition properties of palladium in the plating processing and the stability of the plating bath. The lower limit is preferably 0.01 mg/L or more, more preferably 0.03 mg/L or more, and still more preferably 0.05 mg/L or more. The upper limit of the content of the stabilizer is preferably 10 mg/L or less, more preferably 5 mg/L or less, and still more preferably 1 mg/L or less.

(Other Components)

[0038] In the electroless palladium plating bath according to the present disclosure, various additives usually used in the field of plating bath can be added in addition to the components described above. Examples of such additives include a pH adjuster, a buffer, and a surfactant.

[0039] The pH adjuster is an additive that having the function of adjusting the pH of the plating bath. Examples of the pH adjuster include: acids such as hydrochloric acid, sulfuric acid, nitric acid, citric acid, malonic acid, malic acid, tartaric acid, and phosphoric acid; and alkalis such as sodium hydroxide, potassium hydroxide, and ammonia water. Note that these pH adjusters may be used alone or two or more kinds may be used in a mixture.

[0040] A too low pH tends to lower the rate of depositing palladium, whereas a too high pH may reduce the stability of the electroless palladium plating bath. The electroless palladium plating bath according to the present disclosure may have a pH preferably ranging from 4 to 10, and more preferably from 5 to 8.

[0041] A buffer with a buffering function may be added. Examples of the buffer include: carboxylic acids such as citric acids (e.g., trisodium citrate dihydrate), tartaric acid, malic acid, and phthalic acid; phosphoric acids such as orthophosphoric acid, phosphorous acid, hypophosphorous acid, and pyrophosphoric acid; phosphates thereof such as potassium salts, sodium salts (e.g., trisodium phosphate dodecahydrate), and ammonium salts; boric acid; and tetraboric acid. These buffers may be used alone or two or more kinds may be used in a mixture.

[0042] A surfactant is added as necessary to improve the stability, avoid pits, improve the appearance of the plate, and for other purposes. The surfactant is not particularly limited. Various kinds such as nonionic, cationic, anionic, and amphoteric surfactants can be used.

(Applications)

[0043] The electroless palladium plating bath according to the present disclosure is applicable to, for example, a multilayer plating film including a palladium plating film and a gold plating film. The underlayer on which the palladium plating film is formed is not particularly limited. Examples of the underlayer include: various known base materials such as aluminum (Al), aluminum-based alloys, copper (Cu), and copper-based alloys; and plating films obtained by coating base materials with metal, such as iron (Fe), cobalt (Co), nickel (Ni), copper, zinc (Zn), silver (Ag), gold, platinum (Pt), and alloys thereof, having catalytic properties for reductive deposition of a palladium plating film. Even metal with no catalytic properties can be used as an object to be plated by various methods.

[0044] In addition, the electroless palladium plating bath according to the present disclosure is applicable to an ENEPIG process. In the ENEPIG process, for example, a multilayer plating film (i.e., the electroless nickel/palladium/gold plating film) is obtained which includes a nickel plating film, the palladium plating film described above, and a gold plating film, in this order on aluminum, an aluminum-based alloy, copper, or a copper-based alloy constituting electrodes. Each of the plating films may be formed by a commonly used method.

[0045] Next, a method of producing a multilayer plating film including the palladium plating film formed in the electroless palladium plating bath according to the present disclosure will be described based on the ENEPIG process described above. The conditions for forming the palladium plating film are not limited to those described in the following description and changeable as appropriate based on known techniques.

[0046] The plating conditions and plating equipment for electroless nickel plating using an electroless nickel plating bath are not particularly limited. Various known methods can be selected as appropriate. For example, an object to be plated may be brought into contact with an electroless nickel plating bath at a temperature ranging from 50°C to 95°C for about 15 to 60 minutes. The thickness of the nickel plating film may be set as appropriate in accordance with required characteristics, and usually ranges from about 3 μm to about 7 μm. Various known compositions such as the nickel-phosphorus alloy and the nickel-boron (B) alloy can be used for the electroless nickel plating bath.

[0047] The plating conditions and plating equipment for electroless palladium plating using an electroless palladium plating bath according to the present disclosure are not particularly limited. Various known methods can be selected as appropriate. For example, an object to be plated including a nickel plating film may be brought into contact with an electroless palladium plating bath at a temperature ranging from 50°C to 95°C for about 15 to 60 minutes. The thickness of the palladium plating film may be set as appropriate in accordance with required characteristics, and usually ranges from about 0.001 μm to about 1.0 μm.

[0048] The plating conditions and plating equipment for electroless gold plating using an electroless gold plating bath are not particularly limited. Various known methods can be selected as appropriate. For example, an object to be plated including a palladium plating film may be brought into contact with an electroless gold plating bath at a temperature ranging from 40°C to 90°C for about 3 to 20 minutes. The thickness of the gold plating film may be set as appropriate in accordance with required characteristics, and usually ranges from about 0.001 μm to about 2 μm.

[0049] The electroless palladium plating bath according to the present disclosure is also useful for electronic device components having a plating film. Examples of the electronic device components include components, such as a chip component, a crystal oscillator, a bump, a connector, a lead frame, a hoop material, a semiconductor package, and a printed board, that constitute an electronic device.

<Palladium Plating Film>

[0050] The palladium plating film according to the present disclosure is obtained using the electroless palladium plating bath according to the present disclosure described above. The palladium plating film includes both of a pure palladium film and a palladium alloy plating film containing an alloy component. This is because elements other than palladium may be contained in the palladium plating film depending on the type of the reducing agent to be used. In some cases, components derived from the various additives may also be contained. The rest of the palladium plating film includes palladium and inevitable impurities.

[0051] For example, if formic acid or a salt thereof or hydrazine or a salt thereof is used as the reducing agent, a pure palladium film is obtained. On the other hand, if a phosphoric acid compound such as hypophosphite or phosphite is used as the reducing agent other than the formic acid or the salt thereof, a palladium plating film containing phosphorus is obtained. If a boron compound such as an amine borane compound or a hydroboration compound is used, a palladium plating film containing boron is obtained. If both of a phosphoric acid compound and a boron compound are used, a palladium plating film containing both of phosphorus and boron is obtained.

[EXAMPLES]

[0052] The following describes the invention related to the present application more specifically based on examples and comparative examples. However, the present disclosure is not limited to the following examples at all.

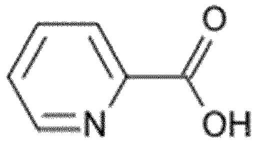
(Examples 1 to 18, Comparative Examples 1 to 8, Reference Example 1)

(Preparation of Plating Bath)

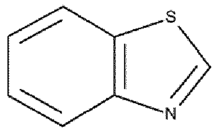
[0053] The plating bath of each of Examples 1 to 18, Comparative Examples 1 to 8, and Reference Example 1 (i.e., an example containing no stabilizer) was prepared by mixing and stirring a palladium compound (i.e., palladium salt), ethylenediamine as the complexing agent, trisodium citrate dihydrate as the buffer, sodium formate as the reducing agent, and a stabilizer at concentrations shown in Tables 2 to 4. The plating bath was set to a temperature (i.e., temperature of the plating processing) of 60°C, and the pH was set to 6.0.

[0054] Chemical formulas of the stabilizers used in Comparative Examples 1 to 8 are as follows.

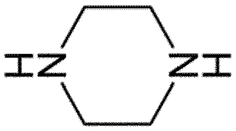
[Chemical 4]



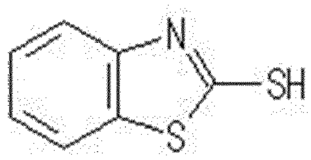
pyridine-2-carboxylic acid



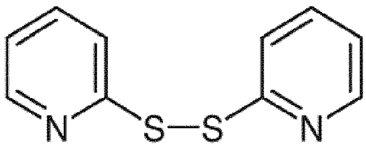
benzothiazole



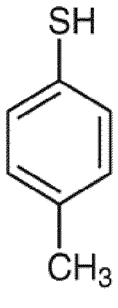
piperazine



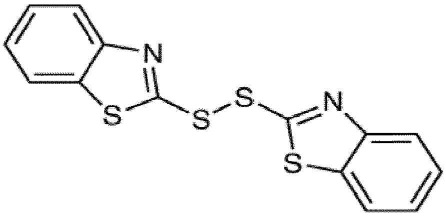
2-mercaptobenzothiazole



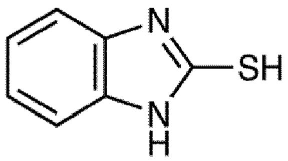
2,2'-dithiodipyridine



4-mercaptotoluene



2,2'-dibenzothiazolyl disulfide



2-mercaptobenzimidazole

(Pretreatment)

[0055] Before forming the electroless plating film, the substrate was subjected sequentially to Pretreatment Steps 1 to 5 shown in Table 1.

[0056] Step 1: Using MCL-16 (trade name: EPITHAS MCL-16 manufactured by C. Uyemura & Co., Ltd.), the substrate (a Si or TEG wafer) was subjected to cleaner treatment.

[0057] Step 2: Then, acid rinse treatment was performed using 30 mass% of a nitric acid solution to form an oxide film on the surface of the substrate.

[0058] Step 3: After that, using MCT-51 (trade name: EPITHAS MCT-51 manufactured by C. Uyemura & Co., Ltd.), the substrate was subjected to primary zincate treatment.

[0059] Step 4: Next, the substrate was subjected to acid rinse treatment using 30 mass% of a nitric acid solution to remove a Zn substitution film, thereby forming an oxide film on the surface of the substrate.

[0060] Step 5: Then, using MCT-51 (trade name: EPITHAS MCT-51 manufactured by C. Uyemura & Co., Ltd.), the substrate was subjected to secondary zincate treatment.

(Plating Processing)

[0061] Next, the substrate subjected to the pretreatment described above was subjected to Plating Processing Step 6 shown in Table 1 to form an electroless nickel plating film on the substrate. More specifically, using a nickel plating bath (trade name: NIMUDEN NPR-18 manufactured by C. Uyemura & Co., Ltd.), electroless plating processing was performed to form an electroless nickel plating film containing phosphorus (a nickel plating film having a concentration of phosphorus in the film ranging from 4% to 8%) on the substrate. Similarly, using a nickel plating bath (trade name: NIMUDEN NLL-1 manufactured by C. Uyemura & Co., Ltd.), electroless plating processing was performed to form a nickel plating film with a low phosphorus content (a nickel plating film having a concentration of phosphorus in the film being less than 4%) on the substrate.

[0062] Next, the substrate having the above-described nickel plating film thereon was subjected to Plating Processing Step 7 shown in Table 1 (i.e., the electroless plating processing using the palladium plating baths of Examples 1 to 18, Comparative Examples 1 to 8, and Reference Example 1) to form a palladium plating film on the surface of the nickel plating film (a pad of 100 μm × 100 μm and a pad of 2 mm × 3 mm) on the substrate.

[Table 1]

			Processing Solution	Processing Temperature	Processing Time (sec)
Pretreatment Step	1	Cleaner	MCL-16	50°C	300
	2	Acid rinse	30 mass% Nitric Acid	21°C	60
	3	Primary Zincate Treatment	MCT-51	21°C	20
	4	Acid rinse	30 mass% Nitric Acid	21°C	60
	5	Secondary Zincate Treatment	MCT-51	21°C	40
Plating Processing Step	6	Electroless Ni (MP-Ni)	NPR-18	80°C	1200
		Electroless Ni (LP-Ni)	NLL-1	90°C	
	7	Electroless Pd	Examples 1-18 Comparative Examples 1-8 Reference Example 1		240

(Measurement of Thickness of Palladium Plating Film)

[0063] Next, using an X-ray fluorescence spectrometer (trade name: XDV-μ manufactured by FISCHER INSTRUMENTS K.K.), the thickness of the palladium plating film formed on each of the pads was measured. The results are shown in Tables 2 to 4.

(Evaluation on Bath Stability)

[0064] Whether or not palladium particles are deposited in the palladium plating bath after the electroless palladium plating processing was visually observed and evaluated under the following criteria. The results are shown in Tables 2 to 4.

○: Even after one week from the plating processing, no deposition of palladium particles was observed.

×: Deposition of palladium particles was observed within one week after the plating processing.

[Table 2]

			Plating Bath Composition								
			Example								
			1	2	3	4	5	6	7	8	9
Pd Salt	Tetraamminepalladium Sulfate (as Pd)	g/L	1.5	1.5					1.5	1.5	1.5
	Tetraamminepalladium Hydrochloride (as Pd)	g/L			1.5	1.5					
	Palladium Sulfate (as Pd)	g/L					1.5				
	Palladium Chloride (as Pd)	g/L						1.5			
Complexing Agent	Ethylenediamine	g/L	4	4	4	4	4	4	4	4	4
Buffer	Trisodium Citrate Dihydrate	g/L	10	10	10	10	10		10	10	10
Reducing Agent	Formic Acid Na	g/L	25	25	25	25	25	25	25	25	25
Stabilizer	2-4-thiazolyl)benzimidazole	mg/L	0.1	1							
	2-methylthio)benzimidazole	mg/L			0.1	0.3					
	2-methylthio)benzothiazole	mg/L					0.2				
	(2-benzothiazolylthio)acetic acid	mg/L						0.2			
	3-2-benzothiazolylthio)propionic acid	mg/L							0.2		
	2-methylthio)pyridine	mg/L								0.2	
	(4-pyridylthio)acetic acid	mg/L									0.2
pH			6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
Processing Temperature			60	60	60	60	60	60	60	60	60

(continued)

			Plating Bath Composition								
			Example								
			1	2	3	4	5	6	7	8	9
Palladium Plating Film Thickness (μm)	Underlayer: Nickel Plating Film with Phosphorus Concentration in Film of 4% to 8%	Pad of 2 mm × 3 mm	0.13	0.11	0.13	0.12	0.13	0.14	0.15	0.14	0.12
		Pad of 100 μm × 100 μm	0.11	0.11	0.12	0.11	0.12	0.12	0.13	0.13	0.09
	Underlayer: Nickel Plating Film with Phosphorus Concentration in Film of Less Than 4%	Pad of 2 mm × 3 mm	0.13	0.10	0.11	0.10	0.14	0.13	0.15	0.13	0.11
		Pad of 100 μm × 100 μm	0.10	0.09	0.09	0.09	0.12	0.11	0.12	0.12	0.07
Stability of Plating Solution			○	○	○	○	○	○	○	○	○

[Table 3]

			Plating Bath Composition								
			Example								
			10	11	12	13	14	15	16	17	18
Pd Salt	Tetraamminepalladium Sulfate (as Pd)	g/L	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
	Tetraamminepalladium Hydrochloride (as Pd)	g/L									
	Palladium Sulfate (as Pd)	g/L									
	Palladium Chloride (as Pd)	g/L									
Complexing Agent	Ethylenediamine	g/L	4	4	4	4	4	4	4	4	4
Buffer	Trisodium Citrate Dihydrate	g/L	10	10	10	10	10	10	10	10	10
Reducing Agent	Formic Acid Na	g/L	25	25	25	25	25	25	25	25	25
Stabilizer	4,4'-dipyridyl sulfide	mg/L	0.4								
	2-methylthio-4-pyrimidinol	mg/L		0.2							
	S-methylthiobarbituric acid	mg/L			0.2						
	4-amino-6-chloro-2-(methylthio)pyrimidine	mg/L				0.2					
	5-(methylthio)-1H-tetrazole	mg/L					0.2				
	5-(ethylthio)-1H-tetrazole	mg/L						0.2			
	5-(benzylthio)-1H-tetrazole	mg/L							0.2		
	N-(phenylthio)phthalimide	mg/L								0.3	
	5-(methylthio)thiophene-2-carboxaldehyde	mg/L									0.4
pH			6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
Processing Temperature			60	60	60	60	60	60	60	60	60

(continued)

			Plating Bath Composition								
			Example								
			10	11	12	13	14	15	16	17	18
Palladium Plating Film Thickness (μm)	Underlayer: Nickel Plating Film with Phosphorus Concentration in Film of 4% to 8%	Pad of 2 mm × 3 mm	0.11	0.13	0.12	0.14	0.16	0.12	0.13	0.12	0.12
		Pad of 100 μm × 100 μm	0.10	0.12	0.11	0.13	0.14	0.12	0.12	0.11	0.08
	Underlayer: Nickel Plating Film with Phosphorus Concentration in Film of Less Than 4%	Pad of 2 mm × 3 mm	0.11	0.12	0.10	0.13	0.16	0.13	0.11	0.13	0.11
		Pad of 100 μm × 100 μm	0.10	0.12	0.08	0.11	0.14	0.11	0.10	0.12	0.08
Stability of Plating Solution			○	○	○	○	○	○	○	○	○

[Table 4]

			Plating Bath Composition								
			Comparative Example								Reference Example
			1	2	3	4	5	6	7	8	1
Pd Salt	Tetraamminepalladium Sulfate (as Pd)	g/L	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
	Tetraamminepalladium Hydrochloride (as Pd)	g/L									
	Palladium Sulfate (as Pd)	g/L									
	Palladium Chloride (as Pd)	g/L									
Complexing Agent	Ethylenediamine	g/L	4	4	4	4	4	4	4	4	4
Buffer	Trisodium Citrate Dihydrate	g/L	10	10	10	10	10	10	10	10	10
Reducing Agent	Formic Acid Na	g/L	25	25	25	25	25	25	25	25	25
Stabilizer	Pyridine-2-Carboxylic Acid	mg/L	10								
	Benzothiazole	mg/L		1.0							
	Piperazine	mg/L			300						
	2-mercaptobenzothiazole	mg/L				0.5					
	2,2’-dithiodipyridine	mg/L					0.5				
	4-mercaptotoluene	mg/L						0.5			
	2,2’-dibenzothiazolyl disulfide	mg/L							0.2		
	2-mercaptobenzimidazole	mg/L								0.2	
pH			6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
Processing Temperature			60	60	60	60	60	60	60	60	60

(continued)

			Plating Bath Composition								
			Comparative Example								Reference Example
			1	2	3	4	5	6	7	8	1
Palladium Plating Film Thickness (μm)	**Underlayer: Nickel Plating Film with Phosphorus Concentration in Film of 4% to 8%**	**Pad of 2 mm × 3 mm**	**0.03**	**0.14**	**0.10**	**0.15**	**0.10**	**0.13**	**0.11**	**0.12**	**0.16**
		Pad of 100 μm × 100 μm	**0.02**	**0.12**	**0.06**	**0.13**	**0**	**0.12**	**0.12**	**0.11**	**0.14**
	Underlayer: Nickel Plating Film with Phosphorus Concentration in Film of Less Than 4%	**Pad of 2 mm × 3 mm**	**0.03**	**0.11**	**0.10**	**0.12**	**0.09**	**0.11**	**0.12**	**0.12**	**0.15**
		Pad of 100 μm × 100 μm	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0.13**
Stability of Plating Solution			×	×	×	×	×	×	×	×	×

[0065] The following is found from Tables 2 and 3: In each of Examples 1 to 18 using, as the stabilizer, an organic compound in which a divalent sulfur compound was bonded to a compound with a heterocyclic structure and which contained neither a thiol group nor a disulfide bond, the thickness of the palladium plating film on the nickel plating film (i.e., the pad of 100 μm × 100 μm and the pad of 2 mm × 3 mm) is maintained as in Reference Example 1 containing no stabilizer. This means that even if a stabilizer is used, a reduction in the deposition properties of palladium is reduced In particular, it is found that even on a nickel plating film having a low phosphorus content (a nickel plating film having a concentration of phosphorus in the film being less than 4%), palladium is sufficiently deposited as on an electroless nickel plating film containing phosphorus (a nickel plating film having a concentration of phosphorus in the film ranging from 4% to 8%).

[0066] In addition, even after one week from the plating processing, no deposition of palladium particles was observed in the plating bath, which shows excellent stability of the plating bath.

[0067] On the other hand, as shown in Table 4, no palladium was deposited at all on the nickel plating film (the pad of 100 μm × 100 μm) having a lower phosphorus content in each of Comparative Examples 1 to 3 using, as a stabilizer, a compound with a heterocyclic structure to which no divalent sulfur compound was bonded, Comparative Examples 4, 6, and 8 using, as a stabilizer, an organic compound in which a divalent sulfur compound was bonded to a compound with a heterocyclic structure and which contained a thiol group, and Comparative Examples 5 and 7 using, as a stabilizer, an organic compound in which a divalent sulfur compound was bonded to a compound with a heterocyclic structure and which contained a disulfide bond. It is also found that deposition of palladium particles was observed in the plating bath within one week after the plating processing, which shows poor stability of the plating bath.

[0068] The present disclosure is particularly advantageously used for a multilayer plating film including a palladium plating film and a gold plating film, and an electroless palladium plating bath used in an ENEPIG process or other processing.

Claims

1. An electroless palladium plating bath at least comprising:

   a palladium compound; a reducing agent; a complexing agent; and a stabilizer,
   the stabilizer being an organic compound in which a divalent sulfur compound is bonded to a compound with a heterocyclic structure, the organic compound containing neither a thiol group nor a disulfide bond.

2. The bath of claim 1, wherein
   the stabilizer has a concentration ranging from 0.01 mg/L to 10 mg/L.

3. The bath of claim 1 or 2, wherein
   the heterocyclic structure is a nitrogen-containing heterocyclic structure or a sulfur-containing heterocyclic structure.

4. The bath of claim 3, wherein
   the compound with the heterocyclic structure is at least one selected from the group consisting of imidazole, imidazolidine, imidazoline, oxadiazole, oxazine, thiadiazole, thiazole, thiazolidine, tetrazole, triazine, triazole, piperazine, piperidine, pyrazine, pyrazole, pyrazolidine, pyridine, pyridazine, pyrimidine, pyrrole, pyrrolidine, benzothiazole, benzimidazole, isoquinoline, thiophene, tetrahydrothiophene, pentamethylene sulfide, and a derivative thereof.

5. The bath of any one of claims 1 to 4, wherein
   the divalent sulfur compound is at least one selected from the group consisting of: thiadiazole, thiazole, thiazolidine, benzothiazole, thiophene, tetrahydrothiophene, methanethiol, benzenethiol, pentamethylene sulfide, dimethyl sulfide, methyl mercaptan, ethyl mercaptan, allyl mercaptan, thiopropionic acid, thioacetic acid, ethyl methyl sulfide, 1-propanethiol, 2-propanethiol, 2-aminoethanethiol, 2-mercaptoethanol, 4-mercaptopyridine, dimethyl sulfoxide, thiazolidine, S-methyl thioacetate, ethyl sulfide, methylpropyl sulfide, 1-butanethiol, thioglycolic acid, 2-(methylthio)ethanol, 3-mercapto-1-propanol, 2-methylthiazoline, cyclopentanethiol, 2-methyltetrahydrothiophene, pentamethylene sulfide, thiomorpholine, S-methyl thiopropionate, 3-mercaptopropionic acid, and a derivative thereof.

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EUROPEAN SEARCH REPORT

Application Number
EP 21 18 7838

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	JP 5 622678 B2 (ISHIHARA CHEMICAL CO LTD; DAIWA FINE CHEMICALS CO LTD LAB) 12 November 2014 (2014-11-12) * paragraph [0005] * * paragraph [0007] * * paragraphs [0011] - [0012] * * paragraphs [0029] - [0030] * * paragraph [0037] * * paragraph [0039] * * paragraph [0041] * * paragraph [0044] * * paragraph [0061] * * paragraph [0072] * -----	1-5	INV. C23C18/44 C23C18/16
A	EP 3 452 635 A1 (ATOTECH DEUTSCHLAND GMBH [DE]) 13 March 2019 (2019-03-13) * paragraph [0010] * * paragraph [0011] * * paragraphs [0033] - [0039] * * paragraphs [0048] - [0053] * * paragraphs [0059] - [0061] * * paragraph [0157] * * paragraphs [0073] - [0089] * -----	1-5	TECHNICAL FIELDS SEARCHED (IPC) C23C
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1 The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	15 December 2021	Crottaz, Olivier

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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EPO FORM 1503 03.82 (P04C01)

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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