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(54) ELECTROLESS PALLADIUM PLATING SOLUTION, AND ELECTROLESS PALLADIUM PLATED COATING

(57) An object of the present invention is to provide an electroless Pd plating solution which enables formation of a Pd plating film forming a plating film having excellent wire bondability even after a high-temperature thermal history. An electroless Pd plating solution of the present invention solved above problems, the solution includes a Palladium compound, at least one selected from a group consisting of a hypophosphorous acid compound and a phosphorous acid compound, at least one selected from the group consisting of an amine borane compound and a hydroboron compound, and a complexing agent.

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Description

TECHNICAL FIELD

[0001] The present invention relates to an electroless palladium plating solution and an electroless palladium plating film.

BACKGROUND ART

[0002] In the electronics industry, electroless nickel electroless palladium immersion gold (ENEPIG), which can add an effect of being excellent in plating film properties such as solder bondability and wire bondability, is commonly used as a method for treating a surface of a circuit of a printed board, or a mounting portion or a terminal portion of an IC package. A plating film obtained by sequentially applying an electroless nickel plating film (hereinafter, sometimes referred to as a "Ni plating film"), an electroless palladium plating film (hereinafter, sometimes referred to as a "Pd plating film") and an immersion gold plating film (hereinafter, sometimes referred to as an "Au plating film") through the ENEPIG process (hereinafter, sometimes referred to as an "electroless Ni/Pd/Au plating film") is commonly used.

[0003] In recent years, a technique has been proposed in which plating film properties are improved by, for example, modifying an electroless palladium plating solution (hereinafter, sometimes referred to as an "electroless Pd plating solution") in order to secure plating film properties required with miniaturization and enhanced density of electronic components.

[0004] For example, Patent Document 1 discloses an electroless Pd plating solution in which as a stabilizer, bismuth or a bismuth compound is used instead of a sulfur compound, resulting in formation of an electroless Pd plating film which has bath stability as high as that achieved with a sulfur compound, and is excellent in corrosion resistance, solder bondability and wire bondability.

PRIOR ART DOCUMENT

PATENT DOCUMENTS

[0005] Patent Document 1: JP4596553B1

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0006] Electroless Ni/Pd/Au plating films which are commonly used exhibit excellent wire bondability before being exposed to a high-temperature thermal history in reflow treatment or the like, but has the problem that wire bondability is significantly deteriorated after the high-temperature thermal history.

[0007] The present invention has been made in view of the circumstances as described above, and an object of the present invention is to provide an electroless Pd plating solution which enables formation of a Pd plating film forming a plating film having excellent wire bondability even after a high-temperature thermal history; and a Pd plating film.

SOLUTION TO PROBLEM

[0008] An electroless Pd plating solution of the present invention solved above problems, the solution includes:

a Palladium compound;
at least one selected from a group consisting of a hypophosphorous acid compound and a phosphorous acid compound;
at least one selected from the group consisting of an amine borane compound and a hydroboron compound; and
a complexing agent.

[0009] Preferable embodiment of the the present inventive electroless Pd plating solution includes any combination of the following options (i) to (iii).

(i) the amine borane compound is at least one selected from a group consisting of dimethylamine borane and trimethylamine borane;
(ii) the hydroboron compound is borohydride salt;

(iii) the complexing agent is at least one selected from a group consisting of ammonia and an amine compound;

[0010] The present invention includes an electroless Pd plating film containing phosphorus; and boron. Preferable embodiment of the present invention includes a laminated film including the electroless Pd plating film and a gold plating film formed on a surface of the electroless Pd plating film.

[0011] The present invention includes an electronic equipment component including the electroless Pd plating film of the present invention.

ADVANTAGEOUS EFFECTS OF INVENTION

[0012] By using the electroless Pd plating solution of the present invention, a Pd plating film forming a plating film having excellent wire bondability even after a high-temperature thermal history in reflow treatment or the like can be obtained.

DESCRIPTION OF EMBODIMENTS

[0013] The present inventors have extensively conducted studies on a cause of a phenomenon in which when a layered plating film with a Au plating film formed on a Pd plating film (hereinafter, sometimes referred to as a "Pd/Au layered plating film") is exposed to a high-temperature thermal history in reflow or the like, the connection success rate in subsequent wire bonding is significantly reduced. Resultantly, it has been considered that exposure to a high-temperature thermal history causes Pd to diffuse to a Au plating film surface, so that a Pd-Au solid solution is formed on the Au plating film surface, resulting in reduction of the connection success rate in wire bonding. One solution for such a problem may be formation of a Au plating film with a large thickness, but this solution leads to a significant increase in cost.

[0014] The present inventors have further conducted studies, and resultantly found that when a Pd plating film containing both P and B (hereinafter, sometimes referred to as a "P-B-Pd ternary alloy film") is formed as an under-layer of the Au plating film, wire bondability after a high-temperature thermal history can be improved. That is, when the Pd plating film contains both P and B, formation of a Pd-Au solid solution on the Au plating film surface can be suppressed even when the film is exposed to a high-temperature thermal history, and as a result, wire bondability more excellent than ever before can be obtained even when the thickness of the film is equivalent to or less than that of a conventional Au plating film.

[0015] AP-B-Pd ternary alloy film having such an effect can be easily formed by using the electroless Pd plating solution of the present invention. Specifically, the electroless Pd plating solution of the present invention is an electroless Pd plating solution containing a palladium compound; at least one selected from the group consisting of a hypophosphorous acid compound and a phosphorus acid compound; at least one selected from the group consisting of an amine borane compound and a hydroboron compound; and a complexing agent.

[0016] A plurality of reducing agents used in the electroless Pd plating solution is known, and these reducing agents include hypophosphorous acid compounds, phosphorous acid compounds, amine borane compounds and hydroboron compounds used for the electroless Pd plating solution of the present invention. However, reducing agents have not used in combination heretofore because when a plurality of reducing agents having different reducing capacities is used, the plating solution has poor stability, so that abnormal precipitation or the like occurs, leading to deterioration of plating film properties. In particular, a hypophosphorous acid compound or a phosphorous acid compound has a sufficient reducing capacity on its own, and does not need to be combined with other reducing agents. However, it has become evident that an inhibitory effect on solid-dissolution of Pd in the Au plating film due to a thermal history cannot be obtained by addition of a single reducing agent or combined use of reducing agents other than those described above, and only the above-described specific combination according to the present invention enables formation of a Pd plating film at a practical level without causing the above-described problems. Such an inhibitory effect on solid-dissolution is a unique effect which can be obtained only by the above-described combination.

Palladium compound

[0017] The palladium compound is a source of palladium ions for obtaining palladium plating. The palladium compound is not limited as long as it is soluble in water, and examples of the palladium compound that can be used include inorganic water-soluble palladium salts such as palladium chloride, palladium sulfate and palladium acetate; and organic water-soluble palladium salts such as tetraaminepalladium hydrochloride, tetraaminepalladium sulfate, tetraaminepalladium acetate, tetraaminepalladium nitrate and dichlorodiethylene diaminepalladium. These palladium compounds may be used alone, or in combination of two or more thereof. The Pd ion concentration in the electroless Pd plating solution is not limited, and when the Pd ion concentration is excessively low, the deposition rate of the plating film may be significantly reduced. On the other hand, when the Pd ion concentration is excessively high, the physical properties of the film may be deteriorated due to abnormal deposition or the like. Therefore, the content of the palladium compound in the plating solution is preferably 0.01 g/L or more, more preferably 0.1 g/L or more, still more preferably 0.3 g/L or more, and even more preferably 0.5 g/L or more, and preferably 10 g/L or less, more preferably 5 g/L or less, still more preferably 3 g/L or less in Pd ion concentration. Pd ions are measured by atomic absorption spectrometry (AAS) using an atomic absorption spectrophotometer.

[0018] In the electroless Pd plating solution of the present invention, in order to exhibit an inhibitory effect on solid-dissolution of Pd, it is necessary that (1) at least one selected from the group consisting of a hypophosphorous acid compound and a phosphorus acid compound (hereinafter, sometimes referred to as a "phosphoric acid compound) be used in combination with (2) at least one selected from the group consisting of an amine borane compound and a hydroboron compound (hereinafter, sometimes referred to as a "boron compound").

(1) At least one selected from the group consisting of a hypophosphorous acid compound and a phosphorous acid compound

[0019] These compounds serve as a source of P to the Pd plating film, and act as a reducing agent for depositing Pd in the electroless Pd plating solution. Examples of the hypophosphorous acid compound include hypophosphorous acid and hypophosphites such as sodium hypophosphite, and examples of the phosphite compound include phosphorous acid and phosphites such as sodium phosphite. The hypophosphorous acid compounds and the phosphorous acid compounds may be used alone, or in combination of two or more thereof. When the content of the hypophosphorous acid compound and/or the phosphorous acid compound in the electroless Pd plating solution is excessively low, the deposition rate during the plating process is reduced, and it may be impossible to obtain a sufficient inhibitory effect on solid-dissolution of Pd in the Au plating film due to a high-temperature thermal history, leading to deterioration of wire bondability. As the content of the hypophosphorous acid compound and the phosphorous acid compound in the electroless Pd plating solution increases, the inhibitory effect on solid-dissolution is improved, but the stability of the electroless Pd plating solution may be deteriorated. The content of the hypophosphorous acid compound and the phosphorous acid compound in the electroless Pd plating solution (a single-compound amount when one compound is contained, and the total amount when two or more compounds are contained) is preferably 0.1 g/L or more, more preferably 0.5 g/L or more, still more preferably 1 g/L or more, even more preferably 2 g/L or more, and preferably 100 g/L or less, more preferably 50 g/L or less, still more preferably 20 g/L or less, even more preferably 15 g/L or less.

(2) At least one selected from the group consisting of an amine borane compound and a hydroboron compound

[0020] These compounds serve as a source of boron to the Pd plating film, and act as a reducing agent for depositing palladium in the electroless Pd plating solution. Examples of the amine borane compound include dimethylamine borane (DMAB) and trimethylamine borane (TMAB), and examples of the hydroboron compound include alkali metal borohydrides such as sodium borohydride (SBH) and potassium borohydride (KBH). In the present invention, it is preferable to use at least one selected from the group consisting of dimethylamine borane, trimethylamine borane, sodium borohydride and potassium borohydride. When the content of the boron compound in the electroless Pd plating solution is excessively low, the deposition rate during the plating process is reduced, and it may be impossible to obtain a sufficient inhibitory effect on solid-dissolution of Pd in the Au plating film due to a high-temperature thermal history, leading to deterioration of wire bondability. As the content of the boron compound in the electroless Pd plating solution increases, the inhibitory effect on solid-dissolution is improved, but the stability of the electroless Pd plating solution may be deteriorated. The content of the boron compound in the electroless Pd plating solution (a single-compound amount when one compound is contained, and the total amount when two or more compounds are contained) is preferably 0.01 g/L or more, more preferably 0.1 g/L or more, still more preferably 0.5 g/L or more, even more preferably 1 g/L or more, and preferably 100 g/L or less, more preferably 50 g/L or less, still more preferably 30 g/L or less, even more preferably 20 g/L or less.

Complexing agent

[0021] The complexing agent has mainly a stabilizing action on the solubility of Pd in the electroless Pd plating solution. The complexing agent may be any of various known complexing agents, and is preferably at least one selected from the group consisting of ammonia and an amine compound, more preferably an amine compound. As the amine compound, methylamine, dimethylamine, trimethylamine, benzylamine, methylenediamine, ethylenediamine, ethylenediamine derivative, tetramethylenediamine, diethylenetriamine, ethylenediaminetetraacetic acid (EDTA), alkali metal salts thereof, EDTA derivatives and glycine. The complexing agents can be used alone, or in combination of two or more thereof. The content of the complexing agent in the electroless Pd plating solution (a single-compound amount when one compound is contained, and the total amount when two or more compounds are contained) may be approximately adjusted so as to obtain the above-described action, and is preferably 0.5 g/L or more, more preferably 1 g/L or more, still more preferably 3 g/L or more, even more preferably 5 g/L or more, and preferably 50 g/L or less, more preferably 30 g/L or less.

[0022] Since the electroless Pd plating solution of the present invention exhibits the above-described effects as long as it has the above-described component composition, the electroless Pd plating solution may have only the component composition. If necessary, the electroless Pd plating solution may contain various additives such as a pH adjuster and a stabilizer may be added.

pH adjuster

[0023] When the pH of the electroless Pd plating solution of the present invention is excessively low, the deposition rate of Pd easily decreases, and when the pH is excessively high, the stability of the electroless Pd plating solution may be deteriorated. The pH is preferably 4 to 10, more preferably 6 to 8. The pH of the electroless Pd plating solution can be adjusted by adding a known pH adjuster. 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. These pH adjusters can be used alone, or in combination of two or more thereof.

Stabilizer

[0024] The stabilizer is optionally added for the purpose of, for example, securing plating stability, improving the appearance after plating, and adjusting the plating film formation rate. The electroless Pd plating solution of the present invention may further contain a known sulfur-containing compound. The sulfur-containing compound is preferably one or more selected from, for example, a thioether compound, a thiocyan compound, a thiocarbonyl compound, a thiol compound, thiosulfuric acid and a thiosulfate. Specific examples thereof include thioether compounds such as methionine, dimethylsulfoxide, thiodiglycolic acid and benzothiazole; thiocyan compounds such as thiocyanic acid, potassium thiocyanate, sodium thiocyanate and ammonium thiocyanate; thiocarbonyl compounds such as thiourea and derivatives thereof; thiol compounds such as cysteine, thiolactic acid, thioglycolic acid, mercaptoethanol and butanethiol; and thiosulfates such as sodium thiosulfate. These sulfur-containing compounds can be used alone, or in combination of two or more thereof. The content of the stabilizer in the electroless Pd plating solution (a single-compound amount when one compound is contained, and the total amount when two or more compounds are contained) may be approximately adjusted so as to obtain an effect such as plating stability, and is preferably 0.1 mg/L or more, more preferably 0.5 mg/L or more, and preferably 500 mg/L or less, more preferably 100 mg/L or less.

[0025] The electroless Pd plating solution of the present invention does not contain a surfactant. When a surfactant is added to the electroless Pd plating solution of the present invention, the surfactant is adsorbed to a surface of the resulting Pd plating film, so that formability of the Au plating film is deteriorated. As a result, wire bondability is deteriorated. The surfactant is any of various known nonionic, cationic, anionic and amphoteric surfactants.

[0026] The present invention includes a Pd plating film which is obtained using the electroless Pd plating solution, and contains P and B. Since the inhibitory effect on solid-dissolution of Pd is obtained as long as the Pd plating film contains both P and B, the content of each of P and B is not limited, and when the content of P or B contained in the Pd plating film increases, the inhibitory effect on solid-dissolution of Pd is further improved. The content of P in the Pd plating film is preferably 0.1% by mass or more, more preferably 0.3% by mass or more, and preferably 10% by mass or less, more preferably 5% by mass or less. The content of B in the Pd plating film is preferably 0.1% by mass or more, more preferably 0.5% by mass or more, and preferably 15% by mass or less, more preferably 10% by mass or less. By appropriately controlling the ratio of P to B, the inhibitory effect on solid-dissolution of Pd is further improved. The mass ratio (P : B) of the content of P and B in the electroless Pd plating film is preferably 10 : 1 to 1 : 10, and more preferably 5 : 1 to 1 : 5. The Pd plating film of the present invention may contain P and B, and further contain components derived from the above-described various additives. The balance consists of Pd and unavoidable impurities.

[0027] The electroless Pd plating solution of the present invention is also suitable for a Pd/Au layered plating film with an Au plating film stacked on a Pd plating film, which is preferably used for plating for bonding of electronic components, etc. Therefore, a layered plating film having the Pd plating film of the present invention and the Au plating film is also a preferred embodiment. The Pd plating film of the present invention can be confirmed to have an inhibitory effect on solid-dissolution of Pd in a Pd/Au layered plating film in which at least a Au plating film is stacked. Therefore, the base that forms the Pd plating film is not limited, and examples thereof include various known base materials such as Al, Al-based alloys, Cu and Cu-based alloys, and plating films in which a base material is covered with a metal catalytic for reduction and deposition of the Pd plating film, such as Fe, Co, Ni, Cu, Zn, Ag, Au, Pt and alloys thereof. Even a noncatalytic metal can be used as an object to be plated in various methods.

[0028] In another preferred embodiment, the electroless Pd plating solution of the present invention can be applied to the ENEPIG process. In the ENEPIG process, an electroless Ni/Pd/Au plating film including the Pd plating film of the present invention can be obtained by forming a Ni plating film, then a Pd plating film, and then a Au plating film on, for example, Al, anAl-based alloy, Cu or a Cu-based alloy that forms an electrode. For the formation of each plating film, a common method may be employed. Hereinafter, a method for producing an electroless Ni/Pd/Au plating film having the Pd plating film of the present invention on the basis of the ENEPIG process will be described, but the conditions for formation of the Pd plating film of the present invention are not limited thereto, and can be appropriately changed on the basis of a known technique.

[0029] The plating conditions and plating apparatus at the time of performing electroless Ni plating using an electroless Ni plating solution are not particularly limited, and any of various known methods can be appropriately selected. For example, an object to be plated may be brought into contact with the electroless Ni plating solution at a temperature of 50 to 95°C for about 15 to 60 minutes. The thickness of the Ni plating film may be appropriately set according to the required properties, and is typically about 3 to 7 μm. Any of various known compositions such as Ni-P alloys and Ni-B alloys can be used for the electroless Ni plating solution.

[0030] The plating conditions and plating apparatus at the time of performing electroless Pd plating using the electroless Pd plating solution of the present invention are not particularly limited, and any of various known methods can be appropriately selected. For example, an object to be plated, on which a Ni plating film is formed, may be brought into contact with the electroless Pd plating solution at a temperature of 50 to 95°C for about 15 to 60 minutes. The thickness of the Pd plating film may be appropriately set according to the required properties, and is typically about 0.001 to 0.5 μm.

[0031] The plating conditions and plating apparatus at the time of performing electroless gold plating using an electroless gold plating solution are not particularly limited, and any of various known methods can be appropriately selected. For example, an object to be plated, on which a Pd plating film is formed, may be brought into contact with the electroless gold plating solution at a temperature of 40 to 90°C for about 3 to 20 minutes. The thickness of the gold plating film may be appropriately set according to the required properties, and is typically about 0.01 to 2 μm.

[0032] When the Pd plating film of the present invention is used, palladium can be inhibited from being diffused to and solid-dissolved in the Au plating film from the Pd plating film due to a thermal history in a mounting process after formation of the film, such as reflow treatment, and therefore excellent wire bondability can be achieved even after the thermal history. The temperature in the thermal history is a temperature at which the mounting process is carried out, and the temperature is not particularly limited. When the Pd plating film of the present invention is used, excellent wire bondability can be achieved even after a thermal history at a high temperature of, for example, 50°C or higher, more preferably 100°C or higher.

Electronic equipment components

[0033] The present invention also includes an electronic equipment component having the plating film. Examples of the electronic equipment component include components that form electronic equipment, such as chip components, crystal oscillators, bumps, connectors, lead frames, hoop materials, semiconductor packages and printed circuit boards. In particular, the plating film is suitably used for a technique for forming UBM (Under Barrier Metal) for solder bonding and wire bonding (W/B) to an A1 electrode or a Cu electrode on a wafer. By stacking an Au plating film on a Pd plating film obtained using the electroless Pd plating solution of the present invention, excellent wire bondability can be achieved even after a thermal history.

[0034] This application claims the benefit of the priority date of Japanese patent application No. 2017-195651 filed on October 6, 2017. All of the contents of the Japanese patent application No. 2017-195651 filed on October 6, 2017 are incorporated by reference herein.

EXAMPLES

[0035] Hereinafter, the present invention will be described in more detail with reference to examples, but the present invention is in no way limited to the following examples, and of course, changes can be appropriately made as long as the above-described and later-described purposes are met. All of these changes are encompassed in the technical scope of the present invention.

[0036] A BGA substrate (Ball Grid Array: Uyemura & Co., Ltd., 5 cm x 5 cm) was sequentially subjected to the pretreatment and plating treatment shown in Table 1, thereby producing test pieces 1 to 20 in which a Ni plating film, a Pd plating film and a Au plating film are formed in this order from the substrate side. The wire bondability of each of the obtained test pieces was examined.

Wire bondability

[0037] Wire bonding was performed using a test apparatus (SemiAutomatic Wire Bonder HB16 manufactured by TPT K.K.), and wire bondability was evaluated at each of 20 points under the following measurement conditions using Bond

Tester SERIES 4000 manufactured by Dage Ltd. The measurement was performed before and after the heat treatment (in which the test piece was held at 175°C for 16 hours). In evaluation of wire bondability, a test piece having an average wire bonding strength of 9.0 g or more after heat treatment was rated "Excellent", a test piece having an average wire bonding strength of 8.5 g or more and less than 9.0 g after heat treatment was rated "Good", a test piece having an average wire bonding strength of 7.5 g or more and less than 8.5 g after heat treatment was rated "Acceptable", and a test piece having an average wire bonding strength of less than 7.5 g after heat treatment was rated "Poor".

[Measurement conditions]

[0038] Capillary: B1014-51-18-12 (manufactured by PECO Ltd.)
Wire: 1mil-Au wire (SPM Ltd.)
Stage temperature: 150°C
Ultrasonic wave (mW): 250 (1st), 250 (2nd)
Bonding time (ms): 200 (1st), 50 (2nd)
Tensile force (gf):25 (1st), 50 (2nd)
Step (1st to 2nd length): 0.7mm
Measurement method: Wire pull test
Equipment: Universal Bond Tester #4000 (manufactured by Nordson Advanced Technology K.K.)
Test speed: 170μm/sec

[Table 1]

	Steps	Name of chemicals	Treatment temperature	Treatment time (min.)	Target film thickness
Pretreatment	Cleaner	ACL-007※1	50°C	5	-
	Soft etching	SPS※1	25°C	1	-
	Pickling	10% H_2SO_4	room temperature	1	-
	Predip	3% H_2SO_4	room temperature	1	-
	activator	MNK-4※1	30°C	2	-
plating treatment	electroless Ni plating	NPR-4※1	80°C	30	6um
	electroless Pd plating	see Table 2			0.1um
	electroless Au plating	TWX-40※1	80°C	13	0.1um
※ 1 available from C. Uyemura & Co., Ltd.					

[Table 2]

Test piece No.			1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Pd salt	tetraamine Pd hydrochloride	[g/L]	2	2	2							2			2	2	2				2	
	tetraamine Pd sulfate	[g/L]				2	2	2					2					2	2			2
	tetraamine Pd nitrate	[g/L]							2	2	2			2						2		
Complexing agent	ethylenediamine	[g/L]	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20
	EDTA·2Na	[g/L]	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20
Reducing agent	formic acid	[g/L]										40				40	40					
	hydrazine	[g/L]											20					20	20	20		
	hypophosphorous acid	[g/L]	10	10	10	10	10	10						25		25					25	25
	phosphorous acid	[g/L]							10	10	10							15				
	dimethylamine borane	[g/L]	10			10			10						20		20					
	trimethylamine borane	[g/L]		10			10			10									20		20	
	sodium borohydride	[g/L]			5			5			5									10		10
pH adjuster	citric acid	[g/L]	30			30				30				30	30		30				30	
	malic acid	[g/L]		30			30		30			30				30			30			
	tartaric acid	[g/L]			30			30			30		30					30		30		30
Additive	sodium thiosulfate	[mg/L]							50		50											
	thioglycolic acid	[mg/L]								50					50					50		
Surfactant	sodium lauryl sulfate	[g/L]																			5	
	polyoxyethylene alkyl ether	[g/L]																				5
Plating bath	Bath temperature	[°C]	55	55	55	55	55	55	55	55	55	60	70	55	50	55	50	60	55	50	55	50
	pH	[-]	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0
Wire pull average strength	before heat treatment	[g]	11.5	11.2	10.9	11.4	11.2	11.2	10.8	11.6	11.2	10.8	11.4	11.4	11.2	11.2	10.9	10.6	11.3	11.4	9.8	9.6
	after heat treatment (175°C for 16 hours)	[g]	9.2	8.9	8.8	9.3	9.0	8.9	9.4	9.2	9.4	7.4	7.3	6.7	7.0	6.9	7.3	7.2	6.9	6.7	5.8	5.4

※Pd salt is Pd ion concentration

[0039] As shown in Table 2, test pieces Nos. 1 to 9 obtained using the electroless Pd plating solution containing a complexing agent, a hypophosphorous acid compound and/or a phosphorous acid compound, and an amine borane compound and/or a hydroboron compound as defined in the present invention were each rated "Good" or "Excellent" in evaluation of wire bondability after heat treatment.

[0040] On the other hand, test pieces Nos. 10 to 18 obtained using a Pd plating solution that did not satisfy the requirements of the present invention were each rated "Poor" in evaluation of wire bondability after heat treatment. Test pieces Nos. 19 and 20 were each rated "Poor" in evaluation of wire bondability after heat treatment because they contained a surfactant.

Claims

1. An electroless Pd plating solution comprising:

a Palladium compound;
at least one selected from a group consisting of a hypophosphorous acid compound and a phosphorous acid compound;
at least one selected from the group consisting of an amine borane compound and a hydroboron compound; and
a complexing agent.

2. The electroless Pd plating solution according to claim 1 wherein,
the amine borane compound is at least one selected from a group consisting of dimethylamine borane and trimethylamine borane; and
the hydroboron compound is borohydride salt

3. The electroless Pd plating solution according to claim 1 or 2 wherein,
the complexing agent is at least one selected from a group consisting of ammonia and an amine compound.

4. An electroless Pd plating film including phosphorus and boron.

5. A laminated film comprising:

the electroless Pd plating film according to claim 4;
a gold plating film formed on a surface of the electroless Pd plating film.

6. An electronic equipment component comprising:

the electroless Pd plating film according to claim 4; or
the laminated film according to claim 5.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2018/036970

A. CLASSIFICATION OF SUBJECT MATTER
Int. Cl. C23C18/44(2006.01)i

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)
Int. Cl. C23C18/00-18/54

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

Published examined utility model applications of Japan	1922-1996
Published unexamined utility model applications of Japan	1971-2018
Registered utility model specifications of Japan	1996-2018
Published registered utility model applications of Japan	1994-2018

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
JSTPlus/JSTChina/JST7580 (JDreamIII)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2011-225927 A (OKUNO CHEMICAL INDUSTRIES CO., LTD.) 10 November 2011, claims, paragraphs [0002]-[0004], [0010]-[0057] & KR 10-2011-0116994 A	1-6
X	JP 2007-9305 A (JAPAN PURE CHEMICAL CO., LTD.) 18 January 2007, claims, paragraphs [0041]-[0063] (Family: none)	4-6
A	JP 2007-98563 A (CENTRAL RESEARCH INSTITUTE OF ELECTRIC POWER INDUSTRY) 19 April 2007, claims, paragraphs [0068]-[0079], [0096]-[0108] (Family: none)	1-6

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"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

Date of the actual completion of the international search 26.11.2018	Date of mailing of the international search report 11.12.2018
Name and mailing address of the ISA/ Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2018/036970

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2000-256866 A (HONMA, Hideo) 19 September 2000 (Family: none)	1-6

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 4596553 B **[0005]**
- JP 2017195651 A **[0034]**