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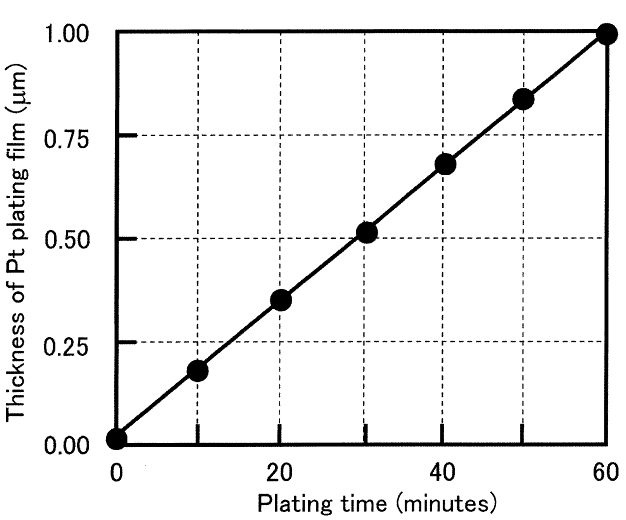
(54) ELECTROLESS PLATINUM PLATING SOLUTION

(57) Provided is an electroless platinum plating solution that can exhibit solution stability without the use of heavy metal ions or thiol compounds and can prevent the generation of ammonia gas. The electroless platinum plating solution is characterized by comprising a water-soluble platinum compound, and one or more reducing agents selected from the group consisting of formalin, glucose, formic acid and formates. The water-soluble platinum compound is preferably one or more water-soluble platinum compounds selected from the group consisting of platinous chloride (II), hydrogen tetrachloroplatinate (II), tetrachloroplatinate (II), platinic chloride (IV), hydrogen hexachloroplatinate (IV), hexachloroplatinate (IV), hydrogen hexahydroxoplatinate (IV), hexahydroxoplatinate (IV) and dichlorotetraammineplatinum (II). The electroless platinum plating solution preferably comprises an organic acid.

[Figure 1]



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Description

[Technical Field]

[0001] The present invention relates to an electroless platinum plating solution.

[Background Art]

[0002] Some electroless platinum plating solutions conventionally known contain dinitrodiammineplatinum or dinitrotetraammineplatinum as a platinum salt, ethylenediamine or ammonia as a complexing agent, and hydrazine monohydrate or sodium borohydride as a reducing agent (See, for example, Patent Literatures 1 to 4).

[0003] Dinitrodiammineplatinum and dinitrotetraammineplatinum are poorly soluble in water. Therefore, they are dissolved in water by adding ethylenediamine or ammonia as a complexing agent to electroless platinum plating solutions containing them to form platinum complexes coordinated with ethylenediamine or ammonia.

[0004] Generally, addition of reducing agents to electroless platinum plating solutions can reduce metal ions or metal complexes on the surface of a plating substrate to deposit metals thereon. Since the platinum complexes coordinated with ethylenediamine or ammonia are resistant to reduction, hydrazine monohydrate or sodium borohydride having a strong reducing action has been added as a reducing agent to the electroless platinum plating solutions. However, since hydrazine monohydrate and sodium borohydride have too strong reducing power, there are problems that platinum is deposited in the plating solutions due to reduction of the platinum complex and the reduction reaction is accompanied by generation of hydrogen.

[0005] Therefore, in order to solve the above problem, the stability of the electroless platinum plating solutions has been improved by adding heavy metal ions such as lead and thallium or thiol compounds as a stabilizer.

[Citation List]

[Patent Literature]

[0006]

[Patent Literature 1] Japanese Patent Laid-Open No. 5-222543
[Patent Literature 2] Japanese Patent Laid-Open No. 9-287078
[Patent Literature 3] International Publication No. WO 2014/162935
[Patent Literature 4] International Publication No. WO 2013/094544

[Summary of Invention]

[Technical Problem]

[0007] However, since heavy metal ions and thiol compounds require the control of the concentration thereof, the plating operation becomes complicated. In addition, the heavy metal ions are harmful to the human body, and they may be co-deposited on the deposited platinum film to lower the film purity. In addition, since ammonia gas is generated from the plating solutions as the prating solutions are used, the working environment deteriorates due to odor associated with the generation of ammonia gas.

[0008] Accordingly, it is an object of the present invention to provide an electroless platinum plating solution that exhibits excellent solution stability even without the use of heavy metal ions or thiol compounds and can prevent the generation of ammonia gas.

[Solution to Problem]

[0009] The present inventors have made intensive studies, and as a result, have found that the conventional electroless platinum plating solutions decrease in solution stability for the following reasons. In the conventional electroless platinum plating solutions, ethylenediamine or ammonia used as a complexing agent is coordinated to platinum ions to form platinum complexes. Since ethylenediamine or ammonia is strongly complexed with platinum ions, a reducing agent having a strong reducing action is required in order to reduce the platinum complexes to deposit them on the surface of substrates to be plated. As a result, the electroless platinum plating solutions are subjected to reduction and decomposition by the reducing power of the reducing agent having a strong reducing action.

[0010] Accordingly, the present inventors have achieved the above object by adopting the following electroless platinum plating solution.

[0011] The electroless platinum plating solution of the present invention is characterized by comprising a water-soluble platinum compound, and one or more reducing agents selected from the group consisting of formalin, glucose, formic acid and formates.

[0012] In the electroless platinum plating solution according to the present invention, the water-soluble platinum compound is preferably one or more water-soluble platinum compounds selected from the group consisting of platinous chloride (II), hydrogen tetrachloroplatinic acid (II), tetrachloroplatinate (II), platinic chloride (IV), hydrogen hexachloroplatinic acid (IV), hexachloroplatinate (IV), hydrogen hexahydroxoplatinic acid (IV), hexahydroxoplatinate (IV) and dichlorotetraammineplatinum (II).

[0013] The electroless platinum plating solution according to the present invention preferably comprises an organic acid as a complexing agent. The organic acid is preferably one or more compounds selected from aliphatic hydroxy acids having a molecular weight of 90 to 500.

[Advantageous Effects of Invention]

[0014] Since a water-soluble platinum compound is used in the electroless platinum plating solution according to the present invention, the platinum compound forms a platinum complex which in turn is easily dissolved in water, even if the electroless platinum plating solution contains no complexing agent such as ethylenediamine or ammonia that is strongly complexed with a platinum ion. The platinum complex formed from the water-soluble platinum compound is more easily reduced than platinum complexes coordinated with ethylenediamine or ammonia, which are formed in conventional electroless platinum plating solutions. Thus, even when formalin, glucose, formic acid or formates having a weak reducing action is used as a reducing agent, the platinum complex can be made to an easily reduced state.

[0015] Any of formalin, glucose, formic acid and formates as reducing agents also have a weaker reducing action than hydrazine monohydrate and sodium borohydride. Thus, the electroless platinum plating solution of the present invention is not decomposed by any of the reducing agents. Therefore, the electroless platinum plating solution of the present invention can provide excellent solution stability even without the use of heavy metal ions or thiol compounds as compared with conventional electroless platinum plating solutions. Any of formalin, glucose, formic acid and formates are also suitable in that they reduce the amount of hydrogen generated than the conventional reducing agents such as hydrazine monohydrate and sodium borohydride.

[0016] Further, since the electroless platinum plating solution of the present invention contains no compound capable of generating ammonia gas such as ethylenediamine or ammonia, it can prevent the generation of ammonia gas.

[Brief Description of the Drawings]

[0017]

[Figure 1] Figure 1 is a graph showing the deposition property exhibited by the electroless platinum plating solution of an embodiment of the present invention.

[Figure 2] Figure 2 is an SEM image of the electroless platinum film obtained by electroless plating processing with the electroless platinum plating solution of Example 1.

[Figure 3] Figure 3 is an SEM image of the electroless platinum film obtained by electroless plating processing with the electroless platinum plating solution of Example 2.

[Description of Embodiments]

[0018] Hereinafter, embodiments of the electroless platinum plating solution according to the present invention will be described.

[1. Electroless platinum plating solution]

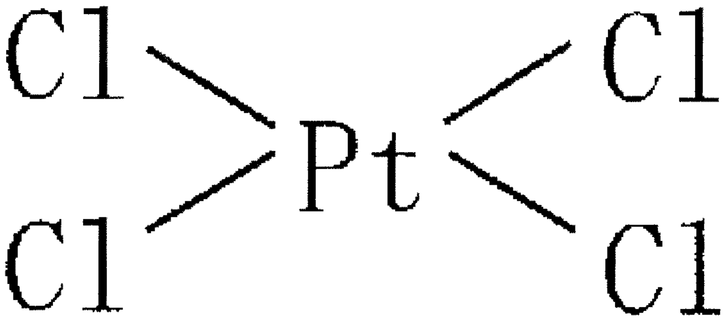
[0019] The electroless platinum plating solution of the present invention is an aqueous solution comprising a water-soluble platinum compound and one or more reducing agents selected from the group consisting of formalin, glucose, formic acid and formates.

[0020] Examples of the water-soluble platinum compound include one or more water-soluble platinum compounds selected from the group consisting of platinous chloride (II), hydrogen tetrachloroplatinic acid (II), tetrachloroplatinate (II), platinic chloride (IV), hydrogen hexachloroplatinic acid (IV), hexachloroplatinate (IV), hydrogen hexahydroxoplatinic acid (IV), hexahydroxoplatinate (IV) and dichlorotetraammineplatinum (II).

[0021] The electroless platinum plating solution of the present invention preferably contains the water-soluble platinum compound in the range of not less than 0.0005 mol/L and not more than 0.05 mol/L and more preferably in the range of not less than 0.0025 mol/L and not more than 0.01 mol/L. When the content of the water-soluble platinum compound in the electroless platinum plating solution is less than 0.0005 mol/L, the electroless platinum film may be difficult to be formed and the plating rate may decrease. When it exceeds 0.05 mol/L, plating itself can be performed well but economic efficiency decreases.

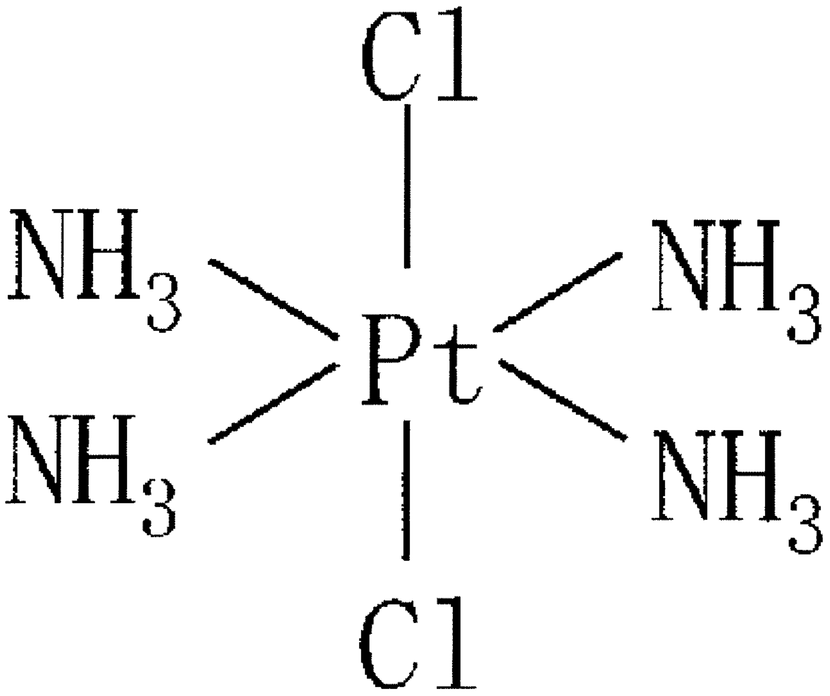
[0022] Platinum chloride (IV) is easily dissolved in the electroless platinum plating solution of the present invention to form a platinum complex represented by the following formula (1).

[Formula 1]



[0023] Dichlorotetraammineplatinum (II) is easily dissolved in the electroless platinum plating solution of the present invention to form a platinum complex represented by the following formula (2).

[Formula 2]



[0024] Both of the platinum complexes represented by the above formulae (1) and (2) are more easily reduced than platinum complexes coordinated with ethylenediamine, which are produced in conventional electroless platinum plating solutions. Thus, the electroless platinum plating solution of the present invention requires no reducing agent having a strong reducing action, and even when a reducing agent having a weak reducing action is used, the platinum complex can be made to an easily reduced state.

[0025] Any of one or more reducing agents selected from the group consisting of formalin, glucose, formic acid and formates have a weak reducing action. However, the reducing agents can make the platinum complexes represented by the above formulae (1) and (2) to an easily reduced state. Any of the above-mentioned reducing agents are advantageous in that they mainly produce carbon dioxide and water as decomposition products accompanying the reduction reaction and reduce the amount of hydrogen generated than hydrazine monohydrate or sodium borohydride. In addition, the electroless platinum plating solution of the present invention is adjusted to a pH range of 6.5 to 12.0 as described below. The above-mentioned reducing agent can be used throughout this pH range.

[0026] The electroless platinum plating solution of the present invention preferably contains the reducing agent in the range of not less than 0.1 mol/L and not more than 1.0 mol/L and more preferably in the range of not less than 0.2 mol /L and not more than 0.8 mol/L. When the content of the reducing agent in the electroless platinum plating solution is less than 0.1 mol/L, undeposited areas may occur. When it exceeds 1.0 mol/L, the reducing action of the reducing agent may become excessive and the solution stability of the electroless platinum plating solution may be thus impaired.

[0027] As the formates, sodium formate, potassium formate and ammonium formate can be used. Sodium formate is suitable due to being readily soluble in water and ease of handling.

[0028] Since the water-soluble platinum compound is used in the electroless platinum plating solution of the present invention, no complexing agent is necessarily required to dissolve the platinum compound in water. However, adding the complexing agent can further stabilize the electroless platinum plating solution.

[0029] It is preferable to use an organic acid as a complexing agent. The organic acid is preferably one or more compounds selected from aliphatic hydroxy acids having a molecular weight of 90 to 500. For example, one or more compounds selected from lactic acid, malic acid, citric acid, trisodium citrate, ammonium citrate, glycine, gluconic acid, malonic acid, oxalic acid, succinic acid, acetic acid, maleic acid and fumaric acid can be used as the organic acid. The complexing agent also acts as a pH buffering material.

[0030] The electroless platinum plating solution of the present invention preferably contains the organic acid in the range of not less than 0.01 mol/L and not more than 0.5 mol/L and more preferably in the range of not less than 0.02 mol /L and not more than 0.3 mol/L. When the content of the organic acid in the electroless platinum plating solution is less than 0.01 mol/L, it may not act as a complexing agent. When it exceeds 0.5 mol/L, plating itself can be performed well but economic efficiency decreases.

[0031] The electroless platinum plating solution of the present invention may further contain various components such as a surfactant, a stress relaxant and a pH adjusting agent.

[0032] Examples of the surfactant that can be used include polyethylene glycol and any other various surfactants conventionally known. In the case of using polyethylene glycol as the surfactant, the wettability of the surface of a plating substrate can be improved, and bubbles can be made easier to separate from the surface of the plating substrate when the bubbles are generated on the surface of the plating substrate.

[0033] Examples of the stress relaxant that can be used include saccharin, 1,4-butynediol, benzenesulfonic acid and naphthalenedisulfonic acid, and any other various stress relaxants conventionally known.

[0034] Examples of the pH adjusting agent that can be used include sodium hydroxide and sulfuric acid. The electroless platinum plating solution can be preferably adjusted in the pH range of 6.5 to 13.0 by adding the adjusting agent. When the pH of the electroless platinum plating solution is less than 6.5, the reducing action of the reducing agent may decrease. Although no particular problem occurs even if the pH of the electroless platinum plating solution exceeds 13.0, pH is preferably not more than 13.0 from the viewpoint of workability such as pH adjustment as well as controlling bath.

[0035] In addition, adjusting the pH of the electroless platinum plating solution in the above-mentioned range can vary the appearance of the resulting electroless platinum film. For example, when the pH of the electroless platinum plating solution is 7, a gray-colored electroless platinum film can be obtained. When the pH is 12, a white-colored electroless platinum film can be obtained.

[0036] According to the electroless platinum plating solution of an embodiment according to the present invention, since a water-soluble platinum compound such as platinous chloride (II), platinic chloride (IV), hexahydroxoplatinate (IV) or dichlorotetraammineplatinum (II) is used, this platinum compound can form a platinum complex even without the use of complexing agents to easily dissolve it in water. In addition, the platinum complex formed from the water-soluble platinum compound is more easily reduced than platinum complexes coordinated with ethylenediamine, which are produced in conventional electroless platinum plating solutions. Thus, even when formalin, glucose, formic acid or formates having a weak reducing action is used as a reducing agent, the platinum complex can be made to an easily reduced state.

[0037] Any of formalin, glucose, formic acid and formates as reducing agents also have a weaker reducing action than hydrazine monohydrate and sodium borohydride. Thus, the electroless platinum plating solution of the present invention is not decomposed by any of the reducing agents. Therefore, the electroless platinum plating solution of the present invention can provide excellent solution stability even without the use of heavy metal ions or thiol compounds as compared with conventional electroless platinum plating solutions. Any of formalin, glucose, formic acid and formates are also suitable in that they reduce the amount of hydrogen generated than the conventional reducing agents such as hydrazine monohydrate and sodium borohydride.

[0038] Further, since the electroless platinum plating solution of the present invention contains no compound capable of generating ammonia gas such as ethylenediamine, it can prevent the generation of ammonia gas.

[2. Electroless plating processing with the electroless platinum plating solution]

[0039] An example of a plating method with the electroless platinum plating solution of the present embodiment will be described below. The example described here uses, as a plating substrate which is an object to be plated, a plating substrate that have a copper film and a nickel film sequentially formed on the surface of an insulating base by electroless plating processing. The plating substrate is not limited to the above-mentioned plating substrate but any conventionally known plating substrate can be used.

[0040] First, the plating substrate is subjected to electrolytic plating processing to form a platinum film (electrolytic platinum film) on the surface of the nickel film.

[0041] Next, the plating substrate having the electrolytic platinum film on the surface of the nickel film is subjected to electroless plating processing by immersing it in an electroless platinum plating solution of the present embodiment. The platinum complex in the electroless platinum plating solution can be reduced and deposited on the surface of the electrolytic platinum film to form another platinum film (electroless platinum film) on the electrolytic platinum film.

[0042] In electroless plating processing with the electroless platinum plating solution of the present embodiment, the deposition rate is 1 to 2 μm/hour, which can be approximately the same deposition rate as that of conventional electroless platinum plating solutions containing dinitrodiammineplatinum or dinitrotetraammineplatinum.

[0043] The working temperature of the electroless platinum plating solution is preferably in the range of 40 to 90°C. When the temperature is less than 40°C, the plating rate may be slow. When the temperature exceeds 90°C, the water evaporation amount may increase and the composition variation may thus increase.

[0044] The time of plating with the electroless platinum plating solution depends on the thickness of the electroless platinum film to be formed. For example, in the case of using an electroless platinum plating solution containing 0.005 mol/L of dichlorotetraammineplatinum (II) (1.0 g/L in terms of platinum) as a water-soluble platinum compound, the plating time of 30 minutes allows an electroless platinum film having a thickness of 0.5 μm to be formed.

[0045] The above-mentioned reducing agent mainly produces carbon dioxide and water with reduction reaction. Since carbon dioxide and water do not accumulate in the electroless platinum plating solution, the electroless platinum plating solution does not deteriorate and can thus be used for a long time.

[3. Uses of the electroless platinum plating solution]

[0046] The electroless platinum plating solution of the present embodiment is suitable for plating electronic components made of metals or the like, electrode materials, synthetic resins such as ABS resins, polyamide resins and polycarbonate resins, ceramics having no conductivity such as alumina and zirconia, and the like. In particular, it can be suitably used for electrodes of oxygen sensors made of ceramics such as zirconia, and the like, as well as various jewelry goods, and the like.

[0047] Hereinafter, the present invention will be described more specifically with reference to the examples, but it will be understood that the present invention is not limited to the following examples.

[Example 1]

[Preparation of plating substrate]

[0048] First, a nickel film having a thickness of 3 μm was formed on a copper plate by electrolytic plating processing. Then, a plating substrate was prepared by forming a platinum film (electrolytic platinum film) having a thickness of 0.1 μm on the surface of the nickel film by electrolytic plating processing.

[Preparation of electroless platinum plating solution]

[0049] In this Example, 0.005 mol/L of dichlorotetraammineplatinum (II) (1.0 g/L in terms of platinum) as a water-soluble platinum compound, 0.5 mol/L of sodium formate as a reducing agent, and 0.1 mol/L of malic acid as an complexing agent were dissolved in water to prepare an electroless platinum plating solution. Next, the pH (at a temperature of 25°C) of the electroless platinum plating solution was adjusted to 7.0 by using sodium hydroxide and sulfuric acid as pH adjusting agents.

[Electroless plating processing]

[0050] The resulting electroless platinum plating solution was warmed to a temperature of 70°C, the plating substrate having the electrolytic platinum film thereon was subjected to electroless plating processing by immersing it in the electroless platinum plating solution to form another platinum film (electroless platinum film) on the electrolytic platinum film.

[0051] At this time, the thickness of the electroless platinum film was measured every 10 minutes until the immersion time reached 60 minutes. The results are shown in Figure 1. From Figure 1, the deposition rate during the electroless plating processing was determined to be 1.0 μm/hour.

[0052] In addition, electroless plating processing was performed for 60 minutes to form an electroless platinum film having a thickness of 0.5 μm. The resulting electroless platinum film was visually observed to be gray-colored. In addition, the surface of the resulting electroless platinum film was observed with a scanning electron microscope (SEM) at a magnification of 30,000 times. As shown in Figure 2, the particle size of the platinum particles was large, and the electroless platinum film has a rough surface shape.

[0053] Then, the temperature of the electroless platinum plating solution was changed to 50°C, 60°C, 70°C or 80°C, and the plating substrate having the electrolytic platinum film formed thereon was subjected to electroless plating processing by immersing it in the electroless platinum plating solution for two hours. At this time, whether platinum deposits were formed in the electroless platinum plating solution or not was observed to determine whether the electroless platinum plating solution was decomposed or not. The results are shown in Table 1. In Table 1, × indicates that the electroless platinum plating solution was decomposed within one hour, Δ indicates that it was decomposed within two hours, and ○ indicates that it was not decomposed at all even after two hours.

[0054] Then, the electroless platinum plating solution kept at a temperature of 50 to 80°C for two hours was allowed to cool naturally, and on the following day, was warmed again to the same temperature. After that, the plating substrate was subjected to electroless plating processing by immersing it in the electroless platinum plating solution for two hours. Even in the electroless platinum plating solution warmed to any of the above temperatures, electroless plating processing was able to be performed normally. This clearly indicates that the electroless platinum plating solution can be used continuously.

[Example 2]

[0055] In this example, the electroless platinum plating solution was prepared in exactly the same manner as in Example 1 except that the pH (at a temperature of 25°C) was adjusted to 11.0.

[0056] The resulting electroless platinum plating solution was warmed to a temperature of 70°C, the plating substrate having the electrolytic platinum film thereon was subjected to electroless plating processing by immersing it in the electroless platinum plating solution for 60 minutes to form an electroless platinum film having a thickness of 0.5 μm on the electrolytic platinum film. The resulting electroless platinum film was visually observed to have a white glossy appearance. In addition, the surface of the resulting electroless platinum film was observed with a SEM at a magnification of 30,000 times. As shown in Figure 3, the particle size of the platinum particles was small, and the electroless platinum film has a smooth surface shape.

[0057] Then, the resulting electroless platinum plating solution was used to determine whether it was decomposed or not, in exactly the same manner as in Example 1. The results are shown in Table 1.

[0058] Then, in exactly the same way as in Example 1, the electroless platinum plating solution kept at a temperature of 50 to 80°C for two hours was processed, and on the following day, electroless plating processing was performed. Even in the electroless platinum plating solution warmed to any of the above temperatures, electroless plating processing was able to be performed normally. This clearly indicates that the electroless platinum plating solution can be used continuously.

[Comparative Example 1]

[0059] In this Comparative Example, the electroless platinum plating solution was prepared in exactly the same manner as in Example 2 except that 0.5 mol/L of hydrazine monohydrate was used instead of sodium formate as a reducing agent. Next, the pH (at a temperature of 25°C) of the electroless platinum plating solution was adjusted to 11.0. Then, the resulting electroless platinum plating solution was used to determine whether it was decomposed or not, in exactly the same manner as in Example 1. The results are shown in Table 1.

[Comparative Example 2]

[0060] In this Comparative Example, the electroless platinum plating solution was prepared in exactly the same manner as in Example 2 except that 0.5 mol/L of sodium borohydride was used instead of sodium formate as a reducing agent. Next, the pH (at a temperature of 25°C) of the electroless platinum plating solution was adjusted to 11.0. Then, the resulting electroless platinum plating solution was used to determine whether it was decomposed or not, in exactly the same manner as in Example 1. The results are shown in Table 1.

[Comparative Example 3]

[0061] In this Comparative Example, the electroless platinum plating solution was prepared in exactly the same manner as in Comparative Example 1 except that 0.005 mol/L of dinitrodiammineplatinum (II) (1.0 g/L in terms of platinum) was used instead of dichlorotetraammineplatinum (II) as a platinum compound. Next, the pH (at a temperature of 25°C) of the electroless platinum plating solution was adjusted to 11.0. Then, the resulting electroless platinum plating solution was used to determine whether it was decomposed or not, in exactly the same manner as in Example 1. The results are shown in Table 1.

[Comparative Example 4]

[0062] In this Comparative Example, the electroless platinum plating solution was prepared in exactly the same manner as in Comparative Example 2 except that 0.005 mol/L of dinitrotetraammineplatinum (II) (1.0 g/L in terms of platinum) was used instead of dichlorotetraammineplatinum (II) as a platinum compound. Next, the pH (at a temperature of 25°C) of the electroless platinum plating solution was adjusted to 11.0. Then, the resulting electroless platinum plating solution was used to determine whether it was decomposed or not, in exactly the same manner as in Example 1. The results are shown in Table 1.

[Table 1]

	Platinum compound	Reducing agent	pH	50° C	60° C	70° C	80° C
Example 1	Dichlorotetraammineplatinum (II)	Sodium formate	7.0	○	○	○	○
Example 2	Dichlorotetraammineplatinum (II)	Sodium formate	11.0	○	○	○	○
Comparative Example 1	Dichlorotetraammineplatinum (II)	Hydrazine monohydrate	11.0	Δ	Δ	×	×
Comparative Example 2	Dichlorotetraammineplatinum (II)	Sodium borohydride	11.0	Δ	Δ	×	×
Comparative Example 3	Dinitroiammineplatinum (II)	Hydrazine monohydrate	11.0	Δ	Δ	×	×
Comparative Example 4	Dinitrodiammineplatinum (II)	Sodium borohydride	11.0	Δ	Δ	×	×

[0063] Table 1 clearly indicates that the electroless platinum plating solutions of both of Examples 1 and 2 in which the platinum compound is dichlorotetraammineplatinum (II) and the reducing agent is sodium formate are not decomposed even after two hours at a temperature ranging from 50 to 80°C and thus have excellent solution stability. On the other hand, it is clear that any of the electroless platinum plating solutions of Comparative Examples 1 to 4 in which the reducing agent is hydrazine monohydrate or sodium borohydride are decomposed within one hour at a temperature ranging from 70 to 80°C, and within two hours even at a temperature ranging from 50 to 60°C and thus has poor solution stability.

[Industrial Applicability]

[0064] As described above, since the electroless platinum plating solution of the present invention has excellent solution stability, it can thus withstand long use. In addition, since the electroless platinum plating solution of the present invention contains no compound capable of generating ammonia gas such as ethylenediamine or ammonia, it can prevent the generation of ammonia gas. Thus, it can prevent the working environment from deteriorating due to odor associated with the generation of ammonia gas. In addition, in the electroless platinum plating solution of the present invention, since no complexing agent such as ethylenediamine or ammonia that is strongly complexed with a platinum ion is used, reducing agents such as formalin, glucose, formic acid and formates that have a weak reducing action can be used. In addition, these reducing agents can reduce the amount of hydrogen gas generated as compared with hydrazine monohydrate and sodium borohydride.

[0065] In addition, the electroless platinum plating solution of the embodiments of the present invention is suitable for plating electronic components made of metals or the like, electrode materials, various synthetic resins, ceramics, and the like. In particular, it can be suitably used for electrodes of oxygen sensors made of ceramics such as zirconia, and the like, as well as various jewelry goods, and the like.

Claims

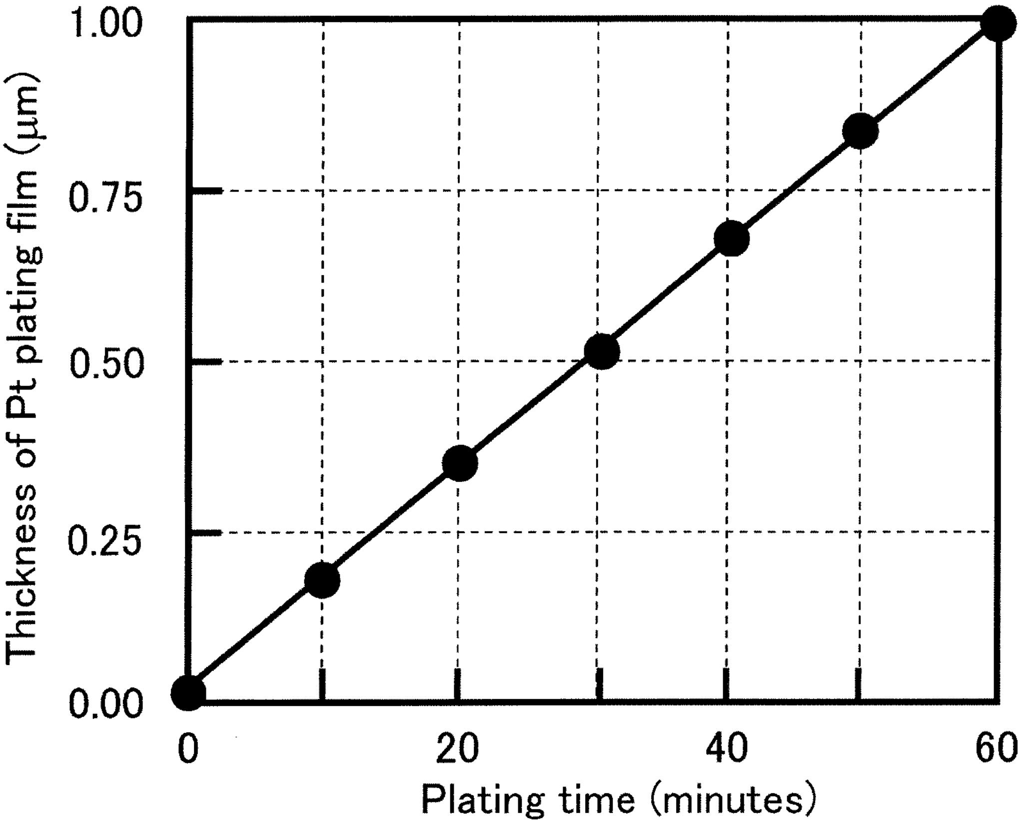
1. An electroless platinum plating solution comprising a water-soluble platinum compound, and one or more reducing agents selected from the group consisting of formalin, glucose, formic acid and formates.

2. The electroless platinum plating solution according to claim 1, wherein the water-soluble platinum compound is one or more water-soluble platinum compounds selected from the group consisting of platinous chloride (II), hydrogen tetrachloroplatinate (II), tetrachloroplatinate (II), platinic chloride (IV), hydrogen hexachloroplatinate (IV), hexachloroplatinate (IV), hydrogen hexahydroxoplatinate (IV), hexahydroxoplatinate (IV) and dichlorotetraammineplatinum (II).

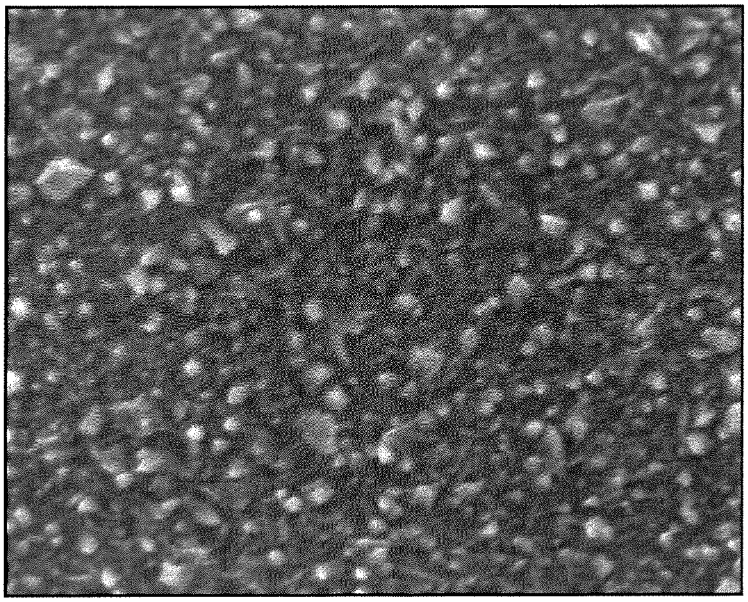
3. The electroless platinum plating solution according to claim 1 or 2, comprising an organic acid as a complexing agent.

4. The electroless platinum plating solution according to any one of claims 1 to 3, wherein the organic acid is one or more compounds selected from aliphatic hydroxy acids having a molecular weight of 90 to 500.

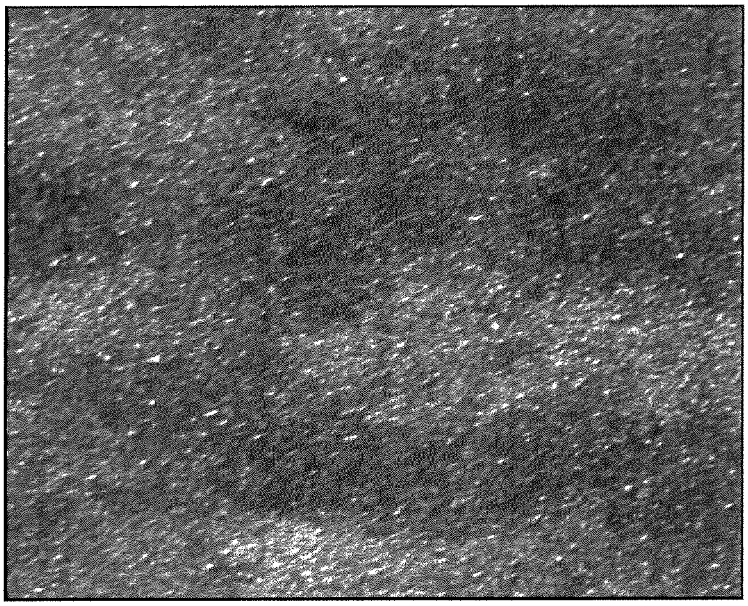
[Figure 1]



[Figure 2]



[Figure 3]



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2016/056047

A. CLASSIFICATION OF SUBJECT MATTER
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)
C23C18/44

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

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Kokai Jitsuyo Shinan Koho	1971-2016	Toroku Jitsuyo Shinan Koho	1994-2016

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JP 54-117329 A (NGK Spark Plug Co., Ltd.), 12 September 1979 (12.09.1979), claims; page 2, lower left column; page 4, upper left column, lines 1 to 16 (Family: none)	1,2 3,4
X	JP 48-56591 A (Toyota Motor Co., Ltd.), 08 August 1973 (08.08.1973), claims; page 3, lower right column, line 12 to lower left column, line 18; page 5, upper left column, lines 1 to 18 & US 3816344 A column 4, line 50 to column 5, line 53; column 6, lines 14 to 34; claims	1-4

☒ 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	"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
"E" earlier application or patent but published on or after the international filing date	"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
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"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
"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	"&" document member of the same patent family

Date of the actual completion of the international search 16 March 2016 (16.03.16)	Date of mailing of the international search report 29 March 2016 (29.03.16)
Name and mailing address of the ISA/ Japan Patent Office 3-4-3,Kasumigaseki,Chiyoda-ku, Tokyo 100-8915,Japan	Authorized officer Telephone No.

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JP 1-319683 A (Electroplating Engineers of Japan Ltd.), 25 December 1989 (25.12.1989), claims; page 2, lower left column, line 8 to lower right column, line 1; page 3, upper left column, line 14 to page 4, upper left column, line 13 (Family: none)	1,2 3,4

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 5222543 A **[0006]**
- JP 9287078 A **[0006]**
- WO 2014162935 A **[0006]**
- WO 2013094544 A **[0006]**