



PLATING METHOD OF HARD DISK SUBSTRATE

BACKGROUND OF THE INVENTION

5 The present invention relates to a method of electroless nickel plating of a glass or ceramic made hard disk substrate.

 In recent years, as substrates for magnetic disks, glass or ceramic made substrates are being used in place of
10 the previously used aluminum made substrates. On such a glass or ceramic made substrate is formed an electroless nickel plating film as a non-magnetic film on which is then formed a magnetic film. In a related art plating method, there have been adopted two methods of electroless nickel
15 plating of a glass or ceramic made substrate. One method includes the steps of dipping a substrate in a sensitizing solution in which stannous chloride is dissolved, to allow stannous ions to adsorb on the substrate; dipping the substrate in an activating solution in which palladium
20 chloride is dissolved, to allow palladium nuclei to deposit on the substrate; and then dipping the substrate in an electroless nickel plating solution. The other method includes the steps of dipping the substrate in a catalyst solution containing stannous chloride and palladium chloride;
25 subjecting the substrate to acceleration treatment (dipping the substrate in an acid or the like), to allow palladium nuclei to deposit on the surface of the substrate; and dipping the substrate in an electroless nickel plating solution.

30 In this way, in both the former sensitizing-activation method and the latter catalyst-acceleration method of electroless nickel plating on a glass or ceramic made hard disk substrate, a tin salt has been used for pre-treatment.

 The present inventors have found that when a glass
35 or ceramic made hard disk substrate is effected to



electroless nickel plating, there is often caused a phenomenon in which pits are formed in an electroless nickel plating film. And, the present inventors have studied the cause of such a phenomenon, and found that the occurrence of the pits is largely affected by the presence of tin remained on the substrate after pre-treatment. To be more specific, tin does not act as any catalyst for electroless nickel plating, and is liable to cause defects such as pits, and further, tin is liable to obstruct plating reaction and finally interrupt the plating reaction if tin ions are accumulated in an electroless nickel plating solution. Therefore, it is desirable to develop a new electroless nickel plating method without using any tin salt for pre-treatment.

SUMMARY OF THE INVENTION

Therefore, an object of the present invention is to provide a method of electroless nickel plating of a glass or ceramic made substrate, in which any tin salt is not used for pre-treatment, to thereby prevent occurrence of pits in an electroless nickel plating film as much as possible.

The present inventors have studied to achieve the above object, and have found that an electroless nickel plating film without occurrence of pits can be formed on a glass or ceramic made substrate by steps of: etching the substrate, conditioning the surface of the substrate using an organic silane compound or a surfactant, dipping the substrate in a catalyst solution which contains a water-soluble palladium salt and an amine type complexing agent such as trimethylamine or glycine, but which does not contain any tin salt, and then dipping the substrate thus pre-treated in an electroless nickel plating solution to form an electroless nickel film, thereby realizing a good electroless nickel deposition without use of any tin salt. The present inventors have also found that in the above method, the

occurrence of pits can be more preferably prevented by rinsing and drying the substrate after the catalyst treatment, and further the occurrence of pits can be more certainly prevented by ultrasonic rinsing the substrate after the above etching treatment and before the above surface conditioning treatment. The present invention has been accomplished on the basis of the above knowledge.

Accordingly, the present invention provides a method of electroless nickel plating of a glass or ceramic disk substrate, including the steps of: conditioning the surface of a glass or ceramic substrate; dipping the substrate in a catalyst solution, the catalyst solution comprising a water-soluble palladium salt and an amine complexing agent, but not containing any tin salt; wherein the mole ratio of water-soluble palladium salt to the amine complexing agent is selected from a range of 1:0.2 to 1:1.5; rinsing and drying the substrate; and subjecting the substrate to electroless nickel plating by dipping the substrate in an electroless nickel plating solution. The above method may further include, before the step of conditioning the surface of the substrate, a step of etching the substrate and then ultrasonic-rinsing the substrate. Also, the above method may further include, after the step of rinsing and drying the substrate, a step of supporting the substrate by a new jig different from that having been used until the step of rinsing and drying the substrate and dipping the substrate in the electroless nickel plating solution using the new jig.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

As a hard disk substrate to be plated in accordance with the method of the present invention, there may be used a known hard disk substrate made from a glass material such as soda glass, aluminosilicate glass or lithium type glass; or a ceramic material.

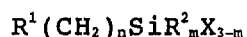
According to the present invention, a glass or ceramic made substrate is cleaned using a cleaner and then etched, as needed.

The cleaner used in the present invention may be one known in the art. The etching solution used for etching treatment may also be one known in the art. Preferably, the etching solution mainly contains a water-soluble fluorine compound such as HF, NaF, KF, or $\text{NH}_4\text{F} \cdot \text{HF}$ in a concentration of 10-50 g/l. Each of the cleaning treatment and the etching treatment can be conducted under the conventional condition in accordance with the conventional method.

According to the present invention, while the above etching treatment is followed by rinsing treatment and surface conditioning treatment, the rinsing treatment may be ultrasonically performed. The ultrasonic rinsing is effective to more certainly prevent occurrence of pits in an electroless nickel plating film. The ultrasonic rinsing may be performed at a temperature of 20 to 40°C for about 1 to 10 minutes using ultrasound with a power of about 0.5-5 W/cm².

The surface conditioning treatment is performed for improving the surface state of a glass or ceramic material used for the substrate. To be more specific, the surface of a glass or ceramic material tends to have negative surface charges and to less adsorb the palladium catalyst having negative charges. The surface conditioning agent used in the present invention is a cationic film forming compound, and may include an organic silane compound or a surfactant such as a nonionic surfactant and cationic surfactant. The surface conditioning agent is dissolved in water to obtain a surface conditioning solution. The surface conditioning agent is used singly or in combination.

Examples of the above organic silane compound include a compound having the following formula:



wherein R^1 is a reactive organic functional group such as a vinyl group, ureido group, amino group, epoxy group,

acryl or methacryl group, or acryloyl or methacryloyl group;

R^2 is a monohydrocarbon group such as an alkyl group having 1 to 8 carbon atoms, preferably 1 to 6 carbon atoms or phenyl group;

5 X is a hydrolyzable group, for example, a halogen atom such as a chlorine atom; an alkoxy group having 1 to 6 carbon atoms such as a methoxy group or ethoxy group; an alkenyloxy group having 2 to 6 carbon atoms such as a vinyloxy group; an alkoxyalkoxy group having 2 to 6 carbon atoms such as a
10 methoxyethoxy group; or a phenoxy group; and

"n" is an integer of 0, 1, 2 or 3, preferably 1, 2 or 3; and "m" is an integer of 0, 1 or 2, preferably 0 or 1.

Examples of the above organic silane compounds include vinylsilane, ureidosilane, aminosilane, epoxysilane, and
15 methacryloxysilane.

Examples of the surfactant for the surface conditioning agent include a nonionic surfactant and a cationic surfactant. The nonionic surfactant includes polyoxyethylene alkylether, polyoxyethylene alkylphenoether, polyoxyethylene
20 alkylester, sorbitan alkylester, and polyoxyethylene sorbitan alkylester. The cationic surfactant includes an aliphatic amine salt such as diethylaminoethyloleidoamide, and amylpolyethylene-polyamide, a quaternary ammonium salt such as an alkyltrimethylammonium salt and alkyl dimethylbenzyl-
25 ammonium chloride, and an alkylpyridinium salt.

The concentration of the above surface conditioning agent may be in a range of 0.01 to 5 g/l, preferably 0.01 to 0.2 g/l, and the pH of the surface conditioning agent is preferably in a range of 2 to 10. The surface conditioning
30 agent may be added with a pH buffer such as potassium hydrogenphthalate, potassium dihydrogenphosphate, boric acid, glycine, sodium citrate, potassium citrate, tartaric acid, lactic acid, acetic acid, or an amine compound; or may be added with ammonia, hydrochloric acid, sodium hydride, or
35 sodium chloride.

The condition for the surface conditioning treatment is not particularly limited; however, in particular, it can be set such that the dipping temperature is in a range of 20 to 60°C, preferably 20 to 40°C, and the dipping time is in a range of 0.5 to 5 minutes, preferably 0.5 to 2 minutes.

After completion of the surface conditioning treatment, the substrate is sequentially subjected to rinsing and catalyst treatment. According to the present invention, as a catalyst solution used for the catalyst treatment, there is used an aqueous solution which mainly contains a water-soluble palladium salt such as palladium chloride or palladium sulfate and an amine type complexing agent, but which does not contain any tin salt.

The amine type complexing agent is a complexing agent for palladium, which includes ammonia, amines, amino-carboxylate, and derivatives thereof. The amine may be monoamines, polyamines such as diamines, triamines and the like, and alkylolamines. Examples of the amine include a monoalkylamine such as methylamine and butylamine; a dialkylamine such as dimethylamine and dibutylamine; a trialkylamine such as trimethylamine and triethylamine; a diamine such as ethylenediamine, tetramethylenediamine and hexamethylenediamine; a triamine such as diethylenetriamine; and an alkylolamine such as diethanolamine and triethanolamine. Examples of the aminocaboxylate include glycine, sodium N,N-diethylglycine salt and derivatives thereof. In this case, the concentration of the water-soluble palladium salt may be in a range of 0.0001 to 0.01 mol/l, preferably 0.0001 to 0.001 mol/l. The ratio of the mol of the water-soluble palladium salt to the mol of the amine type complexing agent may be in a range of 1 : 0.2 to 1 : 1.5, preferably 1 : 0.8 to 1 : 1.2. When the mol ratio is as large as 1 : 2, electroless nickel plating is not well conducted.

The pH of the catalyst solution may be set in a range of 1 to 14. That is to say, the catalyst solution may be acidic or alkaline. According to the present invention, the pH may be preferably set in a range of 6 to 8.

5 The catalyst solution may be incorporated with an alkali metal dihydrogenphosphate salt, sodium hydroxide, hydrochloric acid, or sulfuric acid in a concentration of 0.0001 to 0.05 mol/l as a pH buffering or controlling agent as well as for dissolving the palladium salt in the catalyst
10 solution.

 The condition for dipping the substrate in the catalyst solution may be suitably selected; however, in particular, it may be set such that the temperature is in a range of 20 to 40°C, preferably 20 to 30°C and the dipping time is in a
15 range of 0.5 to 5 minutes, preferably 0.5 to 2 minutes.

 After being dipped in the catalyst solution, the substrate is sequentially subjected to rinsing, drying, and electroless nickel plating.

 The drying treatment is effective to more preferably
20 suppress occurrence of pits, and to improve adhesiveness of the substrate to the palladium nuclei.

 While the substrate to be treated is supported by a jig in the above-described steps, such a jig may be preferably replaced with a new one after the drying treatment (before
25 dipping the substrate in an electroless nickel plating solution). That is to say, it is desirable to dip the substrate in an electroless nickel plating solution using the new jig. If the substrate is dipped in an electroless nickel plating solution while being left supported by the jig having
30 been used in the treatments before the plating treatment, nickel is preferably deposited on the substrate; however, it is simultaneously deposited on the jig as well, and in this case, if the nickel deposited on the jig is fallen off in the plating solution, there may occur an inconvenience that the
35 plating solution is decomposed due to the nickel fragment

fallen off which would act as the nuclei of decomposition.

As an electroless nickel plating solution used for the electroless nickel plating treatment, there may be used a known electroless nickel-phosphorus plating solution using a hypophosphite such as sodium hypophosphite as a reducing agent. For example, there may be used an electroless nickel-phosphorus plating solution mainly containing a water-soluble nickel salt such as nickel sulfate in a concentration of 0.03 to 0.15 mol/l; a complexing agent for the nickel salt, for example, an organic acid salt such as sodium acetate, sodium malate, sodium citrate, an ammonium salt, or an amine in a concentration of 0.05 to 0.5 mol/l; and a reducing agent such as a hypophosphite in a concentration of 0.1 to 0.8 mol/l, wherein the pH is in a range of 4 to 10, particularly 4 to 5. It is preferred to use an electroless nickel plating solution which can deposit a nickel-phosphorus (Ni-P) alloy film having 9 to 13% by weight, preferably 11 to 12.5% by weight of phosphorus and the remaining of nickel. Such a nickel-phosphorus alloy film is amorphous. As the above plating solution, a commercially available plating solution may be used.

The electroless nickel plating treatment may be conducted at a temperature of 80 to 95°C in accordance with the conventional manner, and allows the formation of an electroless nickel plating film (Ni-P alloy film) generally having a thickness of 1 to 30 μm .

Since the above plating method does not use any tin salt for pre-treatment, the occurrence of pits in the plating film obtained by the plating method according to the present invention is prevented as much as possible.

In addition, a magnetic film can be formed on the above electroless nickel plating film in accordance with the conventional manner, to produce a magnetic disk.

EXAMPLE

The present invention will be more fully described with reference to, but not limited to, the following Examples.

5 [Examples and Comparative Examples]

First, a glass made hard disk substrate was cleaned using a cleaner (trade name: Gillite 650, produced by Mangil Co., Ltd.), rinsed and etched. The composition of the etching solution and the etching condition at the etching
10 step are as follows:

Composition of Etching Solution

acidic ammonium fluoride	30 g/l
sulfuric acid	30 cc/l

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Etching Condition

dipping temperature	30°C
dipping time	1 minute

20 Thereafter, the substrate was subjected to electroless nickel plating in accordance with the following steps.

Example 1

Step 1: rinsing
25 Step 2: surface conditioning treatment
Step 3: rinsing
Step 4: catalyst treatment
Step 5: rinsing
Step 6: drying
30 Step 7: electroless Ni-P plating

Example 2

The same steps as those in Example 1 were repeated except that the first rinsing step was ultrasonically
35 performed.

Comparative Example 1

- Step 1: rinsing (ultrasonic rinsing)
- Step 2: catalyst treatment
- Step 3: rinsing
- 5 Step 4: drying
- Step 5: electroless Ni-P plating

Comparative Example 2

- Step 1: rinsing
- 10 Step 2: sensitizing treatment
- Step 3: rinsing
- Step 4: activation treatment
- Step 5: rinsing
- Step 6: drying
- 15 Step 7: electroless Ni-P plating

Comparative Example 3

- Step 1: rinsing
- Step 2: sensitizing treatment
- 20 Step 3: rinsing
- Step 4: activation treatment
- Step 5: rinsing
- Step 6: acceleration treatment
- Step 7: rinsing
- 25 Step 8: drying
- Step 9: electroless Ni-P plating

Comparative Example 4

- Step 1: rinsing
- 30 Step 2: surface conditioning treatment
- Step 3: rinsing
- Step 4: pre-dipping treatment
- Step 5: catalyst treatment (using Sn-containing solution)
- Step 6: rinsing
- 35 Step 7: acceleration treatment

Step 8: rinsing

Step 9: drying

Step 10: electroless Ni-P plating

5 The treatment solution and the treatment condition used
in each step are as follows:

Rinsing

dipping at room temperature for 0.5 minute

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Rinsing (Ultrasonic Rinsing)

dipping at room temperature for 5 minutes

ultrasound

15 Surface Conditioning Treatment

Composition: PCK120I, produced by C. Uyemura & Co., Ltd.
2 cc/l

Condition: dipping at 30°C for 1 minute

20 Catalyst Treatment (Invention)

palladium chloride	0.001 mol/l
glycine	0.001 mol/l
potassium dihydrogenphosphate	0.05 mol/l
NaOH	0.4 mol/l
25 HCl	1.7 cc/l
pH	7
dipping temperature	30°C
dipping time	30 seconds

30 Sensitizing Treatment (Comparison)

stannous chloride	15 g/l
hydrochloric acid	15 cc/l
pH	2
dipping temperature	20°C
35 dipping time	1 minute

Activation Treatment (Comparison)

	palladium chloride	0.15 g/l
	hydrochloric acid	0.15 cc/l
	pH	2
5	dipping temperature	20°C
	dipping time	30 seconds

Acceleration Treatment (Comparison)

	Composition:	AL-106, produced by C. Uyemura & Co., Ltd.
10		100 cc/l
	Condition:	dipping at 25°C for 30 seconds

Pre-dipping Treatment (Comparison)

	NaCl	100 g/l
15	dipping temperature	25°C
	dipping time	30 seconds

Catalyst Treatment (using Sn-containing solution) (Comparison)

	Composition:	AT-105, produced by C. Uyemura & Co., Ltd.
20		30 cc/l
	Condition:	dipping at 30°C for 5 minutes

Drying

	drying temperature	80°C
25	drying time	10 minutes

Electroless Ni-P Plating

	solution:	commercially available electroless nickel
		plating solution using sodium hypophosphite as
30		a reducing agent
		(HDX-7G, produced by C. Uyemura & Co. Ltd.)
	plating temperature:	88°C
	plating time:	100 minutes
	thickness of plating film:	about 12 μ m
35	plating film:	Ni-P film containing 12% by weight of phosphorus

The number of pits occurring in the plating film obtained in each of the above Examples and Comparative Examples were microscopically observed. The results are shown as follows:

5	Example 1:	about 20 pits/135 cm ²
	Example 2:	0 pit/135 cm ²
	Comparative Example 1:	plating impossible
	Comparative Example 2:	100 pits or more/135 cm ²
	Comparative Example 3:	100 pits or more/135 cm ²
10	Comparative Example 4:	100 pits or more/135 cm ²

In each of Examples 1 and 2, the plating film excellent in adhesiveness was formed on the glass made substrate.

As described above, according to the present invention,
15 an electroless nickel plating film excellent in adhesiveness
can be formed on a glass or ceramic made hard disk substrate
without occurrence of defects such as pits.

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CLAIMS

1. A method of electroless nickel plating of a glass or ceramic disk substrate, comprising the steps of:
 - 5 conditioning the surface of a glass or ceramic substrate;
 - dipping the substrate in a catalyst solution, the catalyst solution comprising a water-soluble palladium salt and an amine complexing agent, but not containing any tin salt; wherein the mole ratio of water-soluble palladium salt to the amine complexing agent is selected from a range of 1:0.2 to 1:1.5;
 - 10 rinsing and drying the substrate; and
 - subjecting the substrate to electroless nickel plating by dipping the substrate in an electroless nickel plating solution.
2. The plating method according to claim 1, which further comprises,
 - 15 before said step of conditioning the surface of the substrate, as step of etching the substrate and then ultrasonic-rinsing the substrate.
3. The plating method according to claim 1 or 2, which further comprises, after said steps of rinsing and drying the substrate, a step of
 - 20 supporting the substrate by a new jig different from that having been used for said steps of rinsing and drying the substrate, and then dipping the substrate in the electroless nickel plating solution using the new jig.
4. The plating method of claim 1, wherein the concentration of the
 - 25 water-soluble palladium salt is selected from a range of 0.0001 to 0.01 mol/l.
5. The plating method of claim 4, wherein the concentration of the water-soluble palladium salt is selected from a range of 0.0001 to 0.001 mol/l.
6. The plating method of claim 1, wherein the mole ratio of water-soluble palladium salt to the amine type complexing agent is selected from a
 - 30 range of 1:0.8 to 1:1.2.

7. The plating method of claim 1, wherein the disk substrate is selected from the group consisting of soda glass, aluminosilicate glass, lithium glass and ceramic materials.
- 5 8. The plating method of claim 1, wherein the disk substrate is selected from the group consisting of soda glass, aluminosilicate glass, and lithium glass.
- 10 9. The plating method of claim 1, wherein the amine complexing agent is selected from the group consisting of ammonia, amines, aminocarboxylates and derivatives thereof.
- 15 10. The plating method of claim 9, wherein the amine complexing agent is selected from the group consisting of monoamines, polyamines, and alkylolamines.
11. The plating method of claim 9, wherein the amine complexing agent is selected from the group consisting of glycine and trimethylamine.
- 20 12. The plating method of claim 1, wherein an organic silane compound or a surfactant is used as a conditioning agent in the conditioning the surface of the substrate step.
- 25 13. The plating method of claim 1, wherein a cationic film forming compound is used as a conditioning agent in the conditioning the surface of the substrate step.