(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 3 725 921 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
21.10.2020 Bulletin 2020/43

(21) Application number: **18887864.9**

(22) Date of filing: **14.12.2018**

(51) Int Cl.:
C25D 3/46 *(2006.01)* ***C25D 3/12*** *(2006.01)*
C25D 3/30 *(2006.01)* ***C25D 3/48*** *(2006.01)*

(86) International application number:
PCT/JP2018/046031

(87) International publication number:
WO 2019/117279 (20.06.2019 Gazette 2019/25)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
KH MA MD TN

(30) Priority: **15.12.2017 JP 2017240928**

(71) Applicant: **Takagi, Mikiharu**
Toyohashi-Shi, Aichi 441-8011 (JP)

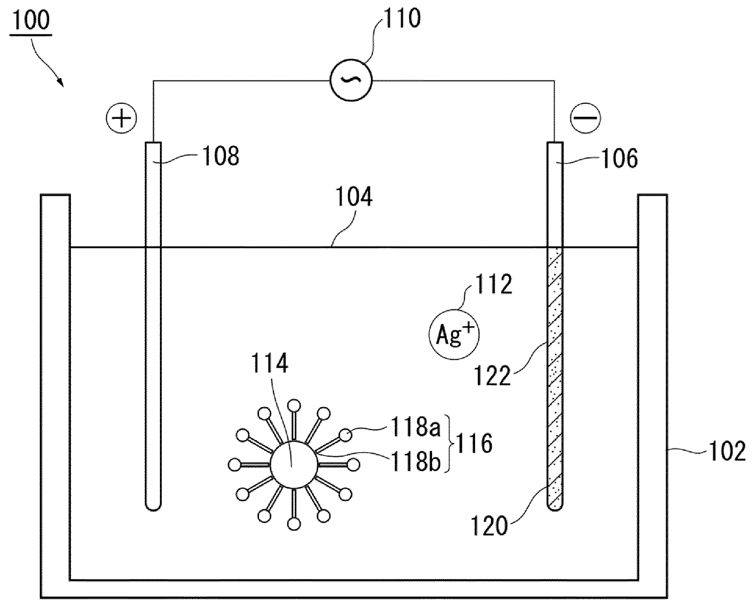
(72) Inventor: **Takagi, Mikiharu**
Toyohashi-Shi, Aichi 441-8011 (JP)

(74) Representative: **Horn Kleimann Waitzhofer**
Patentanwälte PartG mbB
Ganghoferstrasse 29a
80339 München (DE)

(54) METHOD FOR REFINING CRYSTAL GRAINS IN PLATING FILM

(57) In a crystal grain size reduction method for a plating film, electroplating is performed in a condition where ions of a plating metal, a nanocarbon, and an anion based surfactant as a dispersion agent for dispersing the nanocarbon have been blended in a plating solution.

FIG. 1



EP 3 725 921 A1

Printed by Jouve, 75001 PARIS (FR)

Description

TECHNICAL FIELD

[0001] The present invention relates to a method for forming reduced-size crystal grains of a plating film.

RELATED ART

[0002] Composite plating in which small particles have been eutectically deposited in a plating metal film has been known. For example, Patent Document 1 mentions a zinc-nanocarbon composite plating. In this composite plating, a zinc plating film is formed on a plating object by using a zinc plating solution into which nanocarbon and polyacrylamide as a dispersion agent for the nanocarbon have been added.

[0003] Patent Document 1 also mentions that it is preferable that nanocarbon be present in the zinc plating film and that the amount of nanocarbon added into the zinc plating solution be 0.5 to 5.0 g/L. Furthermore, Patent Document 1 indicates that because part of the nanocarbon is exposed out of the zinc plating film, a zinc plating film excellent in sliding characteristic can be made.

RELATED TECHNICAL DOCUMENTS

PATENT DOCUMENTS

[0004] Patent Document 1: JP 2008-214667A

OVERVIEW OF INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0005] It is generally considered that, as in the technology described in Patent Document 1, incorporation of nanocarbon into a plating film will reform the surface of the plating film. For example, the incorporation of nanocarbon into the plating film is considered to harden the plating film and improve the anti-abrasion property associated with sliding.

[0006] Actually, however, it is not that the plating film is made hard but that the nanocarbon particles in a surface layer are hard. Then, the anti-abrasion property of the plating film is not a simple property that depends only on the hardness of the plating film but is affected compositively by carious elements such as the surface roughness (sliding property) and lubricity of plating, and the toughness and crystal grain size of plating metal.

[0007] Concretely, even in the case of a plating metal having high hardness and good sliding property (a plating metal having small crystal grains), because of the hard plating surface, once sliding results in a plating surface (contact surface) having a chip (flaw) formed by galling or the like, the flaw sharply increases the friction coefficient of the plating surface. As a result, the plating surface is further damaged and abrasion rapidly progresses. This phenomenon likely occurs on plating metals that have high hardness but low toughness (plating metals having brittle grain boundaries and weak binding force). On the other hand, in the case of a plating metal having relatively low hardness, chipping does not occur but its low hardness makes the wear rate high and cannot bring about high anti-abrasion property.

[0008] Therefore, it cannot generally be said that incorporation of nanocarbon into a plating film will reform the surface of the plating film. Furthermore, in the case where nanocarbon is incorporated into a plating film, it is very difficult to uniformly disperse the nanocarbon in the plating film or precisely control the amount of the nanocarbon contained in the plating film. Still further, since nanocarbon is a nonconductor, use of a nanocarbon-incorporated plating film on an electrical contact point brings it about that the electrical contact resistance is unstable and greatly increases.

[0009] In view of these problems, it is an object of the present invention to provide a crystal grain size reduction method for a plating film which is capable of reforming the surface of the plating film without substantial incorporation of nanocarbon into the plating film.

MEANS TO SOLVE THE PROBLEM

[0010] As a result of vigorous study to solve the aforementioned problems, the present inventor found that crystal grains of a plating film can be reduced in size by causing nanocarbon to function as if it was a catalyst, while avoiding incorporation of nanocarbon into the plating film, and therefore accomplished the present invention. Specifically, to solve the foregoing problems, a representative construction of a crystal grain size reduction method for a plating film according to the present invention is characterized by performing electroplating in a condition where ions of a plating metal, a nanocarbon, and an anion based surfactant as a dispersion agent for dispersing the nanocarbon have been blended in a plating solution.

[0011] According to the above-described construction, since the dispersion agent is blended in the plating solution, the nanocarbon is dispersed in the plating solution with molecules of the dispersion agent adsorbed to the nanocarbon. Due to the use of an anion based surfactant as a dispersion agent, the nanocarbon dispersed in the plating solution is not readily incorporated into the surfaces of parts to be plated (plating objects) that are connected to the negative electrode. On the surfaces of the plating objects, epitaxial growth of the plating metal proceeds to form crystal grains. The nanocarbon affects the epitaxial growth of the plating metal so as to reduce the size of the crystal grains of the plating film. Although the behavior during this process is not clearly known, it can be speculated that, due to the Brownian motion in the plating solution, nanocarbon particles come into contact with and exert forces to crystal grains, thereby reducing the size of the crystal grains. Thus, the present invention realizes reform of the surface of a plating film by reducing the size of crystal grains of the plating film without substantial incorporation of nanocarbon into the plating film.

[0012] It is appropriate that the nanocarbon be positively charged when in a state of mixture with the plating solution. It is speculated that the nanocarbon positively charged in the plating solution, despite molecules of the anion based surfactant being adsorbed to nanocarbon particles, is attracted to the surface of the part to be plated that is connected to the negative electrode. Due to the attraction to the surface of the part to be plated, the nanocarbon particles can certainly come into contact with and exert forces to crystal grains of the plating film, reliably reducing the size of the crystal grains of the plating film.

[0013] It is appropriate that the particle diameter of the nanocarbon be 2.6 ± 0.5 nm. With the particle diameter of the nanocarbon being in this range, the nanocarbon particles in the plating solution certainly undergo Brownian motion and, when contacting crystal grains of the plating film, exert to the crystal grains appropriate forces that reduces the size of the crystal grains. A reason why the size reduction of the crystal grains becomes insufficient if the particle diameter of the nanocarbon is above the aforementioned range is speculated to be that the Brownian motion of the nanocarbon particles is not sufficient and therefore cannot exert appropriate forces to the crystal grains. Furthermore, a reason why the crystal grain size reduction becomes insufficient if the nanocarbon particle diameter is below the range is speculated to be that, despite occurrence of the Brownian motion, the small masses of the nanocarbon particles cannot exert to the crystal grains a force sufficient for size reduction of the crystal grains.

[0014] It is appropriate that the amount of the nanocarbon added into the plating solution be less than or equal to 0.2 g/L. By setting the amount of the nanocarbon added to a small amount that is less than or equal to 0.2 g/L, the nanocarbon can be prevented from being incorporated into the plating film.

[0015] It is appropriate that the plating metal be silver (Ag), nickel (Ni), tin (Sn), or gold (Au). Therefore, the plating solution that is neutral or weakly acidic may be used.

EFFECT OF THE INVENTION

[0016] According to the present invention, it is possible to provide a crystal grain size reduction method for a plating film which is capable of reforming a surface of a plating film without substantial incorporation of nanocarbon into the plating film.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017]

Fig. 1 is a diagram that generally illustrates a crystal grain size reduction method for a plating film according to an exemplary embodiment of the invention.

Figs. 2A and 2B show microscopic photographs that exhibit a plating film obtained as illustrated in Fig. 1 and a plating film of a comparative example, respectively.

Figs. 3A and 3B are schematic diagrams of the plating films exhibited in Figs. 2A and 2B, respectively.

Figs. 4A and 4B are graphs representing the durabilities and the contact resistances of the plating films exhibited in Figs. 2A and 2B, respectively.

Figs. 5A and 5B show microscopic photographs that exhibit plating films according to another exemplary embodiment of the invention and another comparative example.

DESCRIPTION OF EXEMPLARY EMBODIMENTS

[0018] Exemplary embodiments of the present invention will be described in detail hereinafter with reference to the accompanying drawings. The dimensions, materials, and other concrete numerical values mentioned in conjunction with the following exemplary embodiments are merely illustrative for the sake of easy understanding of the invention and not intended to limit the scope of the invention unless otherwise indicated. In the description and drawings, elements substantially the same in function and construction are indicated by the same reference characters and are not redundantly described. Furthermore, elements and the like that are not directly relevant to the present invention are omitted from graphical representation.

[0019] Fig. 1 generally illustrates a crystal grain size reduction method for a plating film according to an exemplary embodiment. The size reduction method of this exemplary embodiment is carried out by, for example, using a plating apparatus 100. The plating apparatus 100 is an apparatus for carrying out electroplating and includes a container 102, a plating solution 104 in the container 102, a negative electrode 106 and a positive electrode 108 immersed in the plating solution 104, and an electricity source 110 that applies voltage between the two electrodes.

[0020] Blended in the plating solution 104 are ions of a plating metal 112, a nanocarbon 114, and a dispersion agent 116. The plating metal 112 in this example is a monovalent cation of silver (Ag).

[0021] The dispersion agent 116 used in this example is an anion based surfactant. As illustrated in Fig. 1, when molecules of the surfactant are adsorbed to a nanocarbon particle 114, the liphophilic group 118b of each surfactant molecule becomes attached to the nanocarbon particle 114, with the hydrophilic group 118a of each surfactant molecule positioned outward. Therefore, the nanocarbon particles 114 do not aggregate but are dispersed in the plating solution 104 due to the dispersion agent 116.

[0022] As for the nanocarbon 114, for example, the amount added to the plating solution 104 was set to 0.2 g/L, and the particle diameter of the nanocarbon 114 was set to 2.6 ± 0.5 nm. Furthermore, the nanocarbon particles 114 in a mixture with the plating solution 104 are positively charged. The plating solution 104 is neutral because the plating metal 112 is silver (Ag).

[0023] When a plating process is started in the plating apparatus 100 by applying from the electricity source 110 a voltage between the negative electrode 106 and the positive electrode 108, epitaxial growth of the plating metal 112 progresses on the surface of a plating object 120 connected to the negative electrode 106, so that crystal grains of the plating metal 112 form. As a result, the surface of the plating object 120 has on its surface a plating film 122 as indicated by hatching in Fig. 1.

[0024] Figs. 2A and 2B show microscopic photographs of a plating film 122 formed as illustrated in Fig. 1 and a plating film 122A formed as a comparative example. The plating film 122 shown in Fig. 2A was obtained by adding the nanocarbon 114 into the plating solution 104 according to the crystal grain size reduction method of the exemplary embodiment. The plating film 122A of the comparative example shown in Fig. 2B was obtained without adding the nanocarbon 114 into the plating solution 104.

[0025] Observation of the microscopic photographs of the plating films 122 and 122A reveals that the crystal grains of the plating film 122 are clearly smaller than the crystal grains of the plating film 122A. Therefore, it is clear that the crystal grain size reduction method of this exemplary embodiment is capable of reducing the size of the crystal grains (forming nanocrystal grains) of the plating film 122. Table 1, presented below, compares the carbon contents of the plating films 122 and 122A.

Table 1

Addition of nanocarbon	Carbon content of plating film (mass%)
No	0.00182
Yes	0.00178

[0026] As mentioned in Table 1, the carbon content of the plating film 122 according to this exemplary embodiment in which the nanocarbon 114 was added was substantially the same as the carbon content of the plating film 122A of the comparative example in which the nanocarbon 114 was not added. Thus, it is clear that the plating film 122 formed by the crystal grain size reduction method of the exemplary embodiment did not substantially incorporate the nanocarbon 114.

[0027] Thus, in the crystal grain size reduction method according to the exemplary embodiment, size reduction of the crystal grains of the plating film 122 is achieved by the nanocarbon 114 functioning as if it was a catalyst, without substantial incorporation of the nanocarbon into the plating film 122. This phenomenon will be discussed below.

[0028] First of all, the nanocarbon 114 dispersed in the plating solution 104 is not readily incorporated into the plating film 122 on the surface of the plating object 120 that is connected to the negative electrode 106 because an anion based surfactant is used as the dispersion agent 116. In addition, since the amount of the nanocarbon 114 added is as small as 0.2 g/L, incorporation of the nanocarbon 114 into the plating film 122 does not easily occur in the first place. Thus, in the conditions as indicated above, the nanocarbon 114 was, actually, hardly incorporated into the plating film 122.

[0029] Next, it is speculated that, because the nanocarbon particles 114 are positively charged in the plating solution 104, the molecules of the anion based surfactant adsorbed to the nanocarbon particles 114 do not prevent the nanocarbon particles 114 from being attracted to the surface of the plating object 120 connected to the negative electrode 106, so that the nanocarbon particles 114 affect the epitaxial growth of the plating metal 112.

[0030] Although the behavior of the nanocarbon particles 114 during this process is not clearly known, it can be speculated that, due to the Brownian motion in the plating solution 104, the nanocarbon particles 114 come into contact with and exert forces to crystal grains, thereby achieving size reduction of the crystal grains. Specifically, it can be speculated that the positively charged nanocarbon 114 in the plating solution 104 is attracted to the surface of the plating object 120 so as to certainly come into contact with and exert forces to crystal grains of the plating film, so that the crystal grains of the plating film can be certainly reduced in size.

[0031] Furthermore, since the particle diameter of the nanocarbon 114 is set within the range of 2.6 ± 0.5 nm, the particles of the nanocarbon 114 in the plating solution 104 certainly undergo Brownian motion, so that as nanocarbon particles 114 come into contact with crystal grains of the plating film, the nanocarbon particles 114 exert to the crystal grains appropriate forces that reduce the size of the crystal grains. A reason why the size reduction of the crystal grains becomes insufficient if the particle diameter of the nanocarbon 114 is above the aforementioned range is speculated to be that the Brownian motion of the nanocarbon particles is not sufficient and therefore cannot exert appropriate forces to the crystal grains. On the other hand, a reason why the crystal grain size reduction becomes insufficient if the particle diameter of the nanocarbon 114 is below the range is speculated to be that, despite occurrence of the Brownian motion, the small masses of the nanocarbon particles cannot exert to the crystal grains a force sufficient to reduce the size of the crystal grains.

[0032] By the way, the plating object 120 provided with the plating film 122 is used as an electrical contact. Therefore, the plating film 122 is required to have a low electric resistivity (contact resistance). Furthermore, since the plating object 120 is repeatedly inserted into a socket or the like, the plating film 122 is also required to be high in durability (i.e., the anti-abrasion property associated with sliding).

[0033] A crystal structure of a metal will be described with reference to Figs. 3A and 3B. Figs. 3A and 3B are schematic diagrams that correspond to the plating films 122 and 122A shown in Figs. 2A and 2B.

[0034] The metal can be viewed as a crystal grain aggregate which includes crystal grains and grain boundaries that surround the crystal grains (defects of crystals or impurities) and in which crystal grains are bound to each other at grain boundaries. The abrasion of metal caused by sliding occurs in two different ways: crystal grains themselves undergo transgranular fracture; and boundaries fracture and the metal chips and erodes in block units of crystal grains. In this exemplary embodiment, it is an object to restrain the grain boundary fracture in which the metal chips off grain by grain and therefore increase the durability. In metal, when grain boundary fracture involves erosion of large crystal grains, the chipped-off volume, that is, the amount of erosion, is large; on the other hand, erosion of a small crystal grain means a small amount of erosion. Furthermore, in metal, since crystal grains are bound together at grain boundaries, it is speculated that the greater the strength of grain boundaries and the binding force thereof, the less easily erosion occurs. Therefore, crystal structure features of a metal that are needed in order to realize a highly durable plating film are that the crystal grains are small and that the binding force at grain boundaries that binds crystal grains together is strong.

[0035] In the plating film 122 illustrated in Fig. 3A, the crystal grains 124 are smaller than the crystal grains 124A of the plating film 122A illustrated in Fig. 3B and the grain boundaries 126 where crystal grains 124 are bound together outnumber the grain boundaries 126A of the plating film 122A. Therefore, the plating film 122 is less easily erodable to sliding and therefore more durable than the plating film 122A.

[0036] Still further, it is generally considered that metal becomes harder as the crystal grains are made smaller. In this regard, the plating film 122A of the comparative example, in which the crystal grains 124A were not reduced in size, had a Vickers hardness of 90 to 110 Hv. On the other hand, the plating film 122 of the exemplary embodiment, in which the crystal grains 124 were reduced in size, had a Vickers hardness of 100 to 110 Hv, making it clear that size reduction of the crystal grains 124 does not make the plating film 122 harder. Therefore, good running-in property (lubricity) of the contact surface characteristic of silver (Ag), which is the plating metal 112, can be maintained, so that the surface of the plating film 122 (the contact surface at the time of sliding) is smooth and the friction coefficient does not considerably change even after repeated sliding. Thus, the durability of the plating film 122 can be increased.

[0037] Next, the electrical contact resistance of the plating film 122 will be described. It is considered that when the crystal grains of metal are made smaller, grain boundaries generally increase, so that the electrical contact resistance increases. However, in the plating film 122 according to the exemplary embodiment, although the crystal grains 124 are small, the contact resistance is not high but about 3×10^{-6} to about 3.5×10^{-6} $\Omega\cdot$cm. Incidentally, the contact resistance of a super hard silver plating that has substantially the same crystal grain diameter is as high as greater than or equal to 8×10^{-6} $\Omega\cdot$cm. A reason for this is speculated to be that because the size reduction of the crystal grains 124 of the plating film 122 does not involve the alloying with a different metal, such as antimony (Sb), or because no adsorbent organic luster is used in the plating film 122, the grain boundaries 126 contain only a small amount of impurities.

[0038] Figs. 4A and 4B are graphs indicating the durability and the contact resistance of the plating films 122 and 122A illustrated in Figs. 2A and 2B, respectively. In each one of the graphs in Figs. 4A and 4B, the horizontal axis represents the number of back-and-forth movements (number of sliding movements) and the vertical axis represents the friction force (N) or the resistance value (mΩ). Note that high friction forces, meaning high friction coefficient, are considered to mean that abrasion of the surface easily progresses and the anti-abrasion property thereof, that is, the durability thereof, is low.

[0039] The plating film 122 described in Fig. 4A produces a smaller friction force as a whole than the plating film 122A described in Fig. 4B, and therefore is higher in anti-abrasion property. In fact, the plating film 122 remained unfractured even when the number of back-and-force movements reached 1000. On the other hand, the plating film 122A, being low in anti-abrasion property, was destroyed as exhibited in Fig. 4B when the number of back-and-force movements was about 600. Furthermore, the plating film 122 exhibited stable electrical resistance at low resistance values, compared with the plating film 122A. On the other hand, the plating film 122A exhibited unstable electrical resistance values as a whole. Furthermore, the resistance value of the plating film 122A rapidly increased as the plating film 122A was fractured at the time of about 600 back-and-forth movements.

[0040] Thus, it was made clear that the plating film 122 formed by the crystal grain size reduction method according to the exemplary embodiment was lower in contact resistance and higher in durability than the plating film 122A of the comparative example, in which nanocarbon 114 was not added into the plating solution 104. That is, in the crystal grain size reduction method according to the exemplary embodiment, reform of the surface of the plating film 122 is realized by reducing the size of the crystal grains of the plating film 122 without substantial incorporation of the nanocarbon 114 into the plating film 122 although the nanocarbon 114 is added into the plating solution 104.

[0041] Examples and comparative examples in which different amounts of the nanocarbon 114 were added will be described below. Table 2 describes Examples 1 and 2 and Comparative Examples 1 and 2. In Examples 1 and 2, the amounts of the nanocarbon 114 added were 0.1 g/L and 0.2 g/L, respectively. In Comparative Example 1, the amount of the nanocarbon 114 added was zero, that is, no nanocarbon 114 was added. In Comparative Example 2, the amount of the nanocarbon 114 added was 0.3 g/L.

Table 2

	The amount of nanocarbon added (g/L)	Evaluations		
		Size of crystal grains	Anti-abrasion property	Volume resistance
Comparative Example 1	0	Large	No good and soft	Low
Example 1	0.1	Quite small	Acceptable	Low
Example 2	0.2	Quite small	Acceptable	Low
Comparative Example 2	0.3 or larger	Intermediate	Acceptable	High

[0042] As mentioned in Table 2, in Comparative Example 1 with no nanocarbon 114 added into the plating solution 104, the size of the crystal grains of the plating film was "Large", the anti-abrasion property (durability) thereof was "No good", and the volume resistance (electrical resistance) thereof was "Low". In Comparative Example 2 with the amount of the nanocarbon 114 added being greater than or equal to 0.3 g/L, the size of the crystal grains of the plating film was "Intermediate", the anti-abrasion property thereof was "Acceptable", and the volume resistance thereof was "High". In contrast, in both Examples 1 and 2 with the amount of the nanocarbon 114 added being less than or equal to 0.2 g/L, the size of the crystal grains of the plating film was "Quite small", the anti-abrasion property thereof was "Acceptable", and the volume resistance thereof was "Low". Therefore, it is clear that if the amount of the nanocarbon 114 added is less than or equal to 0.2 g/L, the size of the crystal grains of the plating film 122 can be made quite small and the anti-abrasion property thereof can be made high and, furthermore, the volume resistance thereof does not increase but remains low despite the quite small size of the crystal grains.

[0043] Figs. 5A and 5B show microscopic photographs exhibiting a plating film 128 according to another exemplary embodiment and a plating film 128A of another comparative example. The plating film 128 according to the another exemplary embodiment exhibited in Fig. 5A is different from the above-described plating film 122 in that the plating metal 112 of the plating film 128 was nickel (Ni) instead of silver (Ag). The plating film 128A of the another comparative example exhibited in Fig. 5B was obtained by using as the plating metal 112 nickel (Ni) instead of silver (Ag) and by omitting addition of the nanocarbon 114 into the plating solution 104. Note that, due to the use of nickel (Ni) as a plating metal, the plating solution 104 was weakly acidic.

[0044] Observation of the microscopic photographs of the plating films 128 and 128A reveals that the crystal grains of the plating film 128 are clearly smaller than the crystal grains of the plating film 128A. Therefore, it is clear that the crystal grain size reduction method according to the another exemplary embodiment is able to reduce the size of the crystal grains of the plating film 128. Table 3, presented below, indicates results of a sliding test of the plating films 128 and 128A.

Table 3

Load (g)	Number of slidings	
	Nickel sulfamate	+ Nanocarbon
50	434.35	520.55
50	426.91	513.61
50	423.91	526.31
50	426.9	523.30
50	423.88	529.15
50	416.68	526.33
Average	425.4	523.2

[0045] The plating film 128A of the comparative example was formed by blending nickel sulfamate in the plating solution 104 and omitting addition of the nanocarbon 114 into the plating solution 104. As indicated in Table 3, the plating film 128A was subjected to repeated sliding with a load of 50 g and was destroyed when the number of sliding cycles reached, averagely, 425.4.

[0046] On the other hand, the plating film 128 according to the another exemplary embodiment was formed by blending nickel sulfamate in the plating solution 104 and adding the nanocarbon 114 into the plating solution 104. As indicated in Table 3, the plating film 128 was destroyed when the number of sliding movements reached, averagely, 523.2. This clarifies that the plating film 128 was more durable than the plating film 128A of the another comparative example.

[0047] Therefore, by the size reduction method according to this exemplary embodiment, reform of the surfaces of the plating films 122 and 128 can be realized by making the crystal grains of the plating films 122 and 128 quite small without incorporation of the nanocarbon 114 into the plating films 122 and 128, respectively.

[0048] Incidentally, although in the foregoing exemplary embodiments of the invention, the plating metal 112 is silver (Ag) or nickel (Ni) as an example, this is not restrictive. The plating metal 112 may also be tin (Sn) or gold (Au). In such cases, it is speculated that the crystal grains of the plating film can be made quite small to reform the surface of the plating film by causing the nanocarbon 114 to function as if the nanocarbon 114 was a catalyst, while avoiding incorporation of the nanocarbon 114 into the plating film.

[0049] While the exemplary embodiments of the invention have been described with reference to the drawings, it should be apparent that the invention is not limited by the foregoing examples or the like. It should be understood that a person having ordinary skill in the art can conceive various changes and modifications within the scope described in the appended claims and that such changes and modifications belong to the technical scope of the present invention.

INDUSTRIAL APPLICABILITY

[0050] The invention can be utilized as a method for forming reduced-size crystal grains of a plating film.

LIST OF REFERENCE NUMERALS

[0051]

100	... plating apparatus
102	... container
104	... plating solution
106	... negative electrode
108	... positive electrode
110	... electricity source
112	... plating metal
114	... nanocarbon
116	... dispersion agent
118a	... hydrophilic group

118b ... lipophilic group
120 ... plating object
122, 122A, 128, 128A ... plating film
124, 124A... crystal grains
126, 126A... grain boundaries

Claims

1. A crystal grain size reduction method for a plating film comprising
   performing electroplating in a condition where ions of a plating metal, a nanocarbon, and an anion based surfactant as a dispersion agent for dispersing the nanocarbon have been blended in a plating solution.

2. The crystal grain size reduction method according to claim 1, wherein the nanocarbon is positively charged when in a state of mixture with the plating solution.

3. The crystal grain size reduction method for the plating film according to claim 1 or 2, wherein the plating metal is silver, nickel, tin, or gold.

FIG. 1

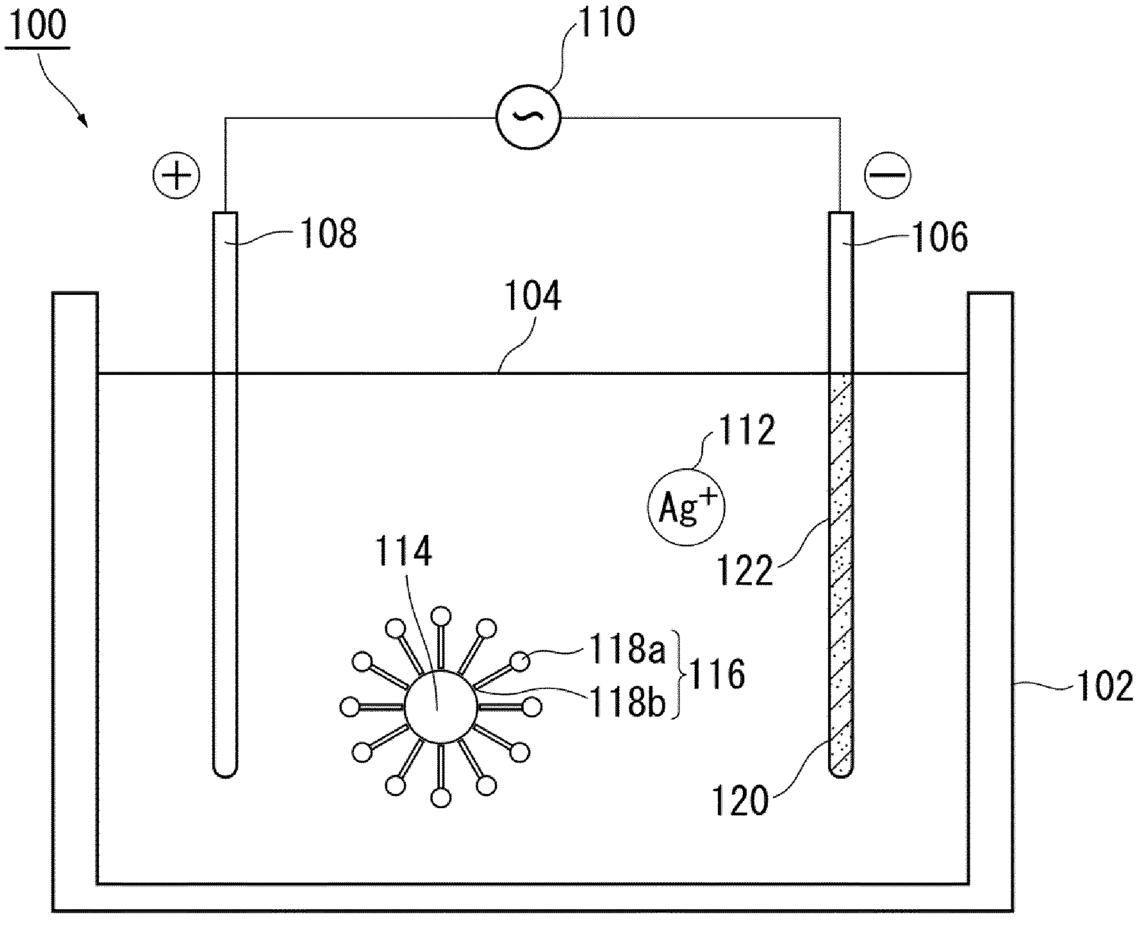
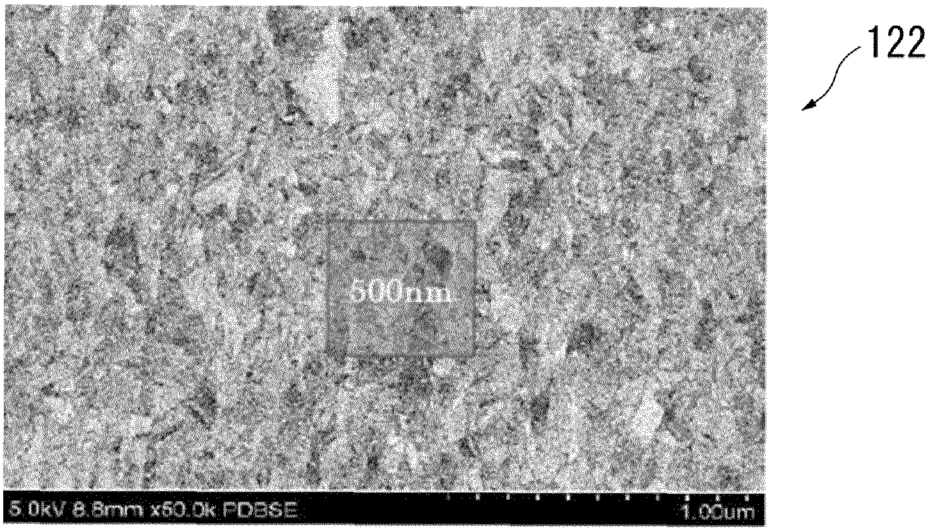
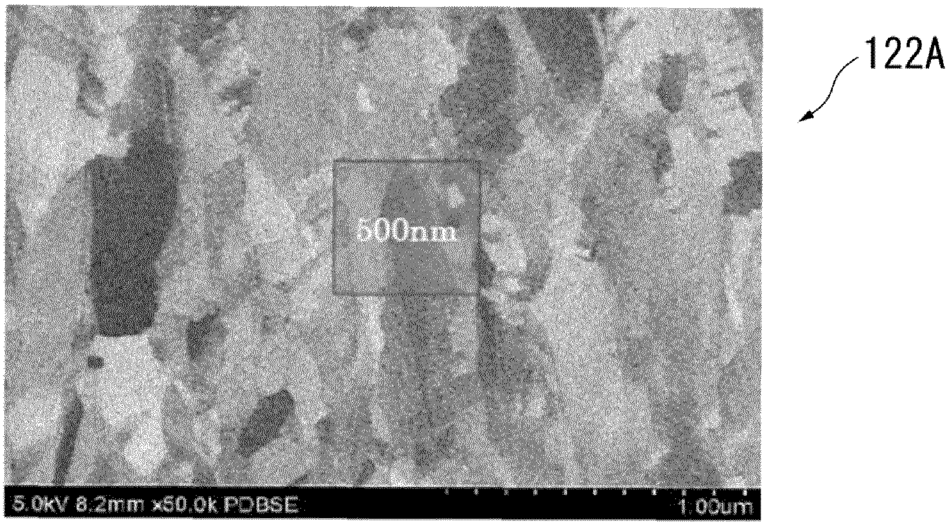


FIG. 2A



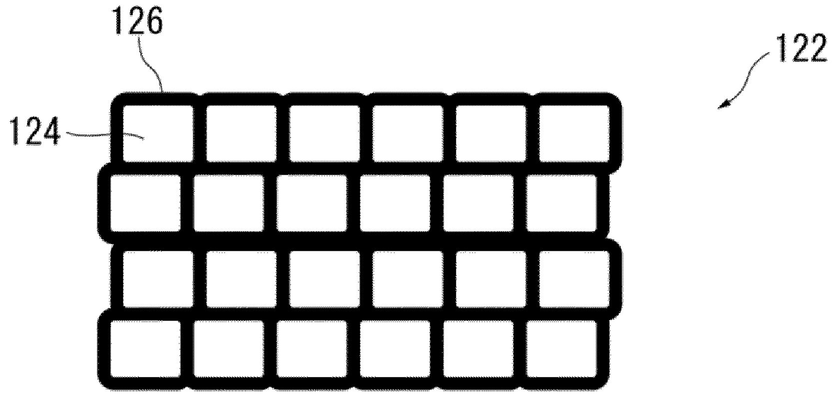
(a)

FIG. 2B



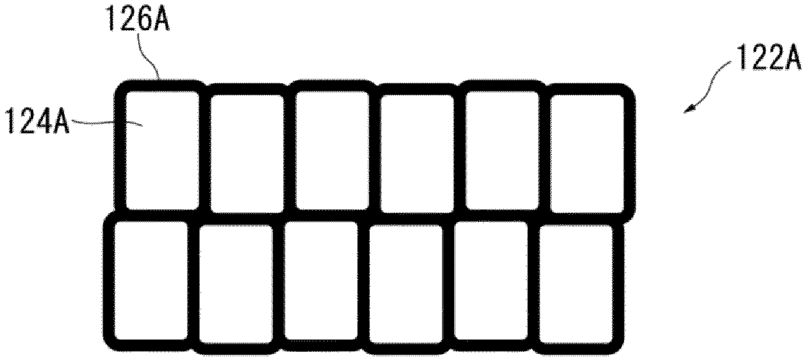
(b)

FIG. 3A



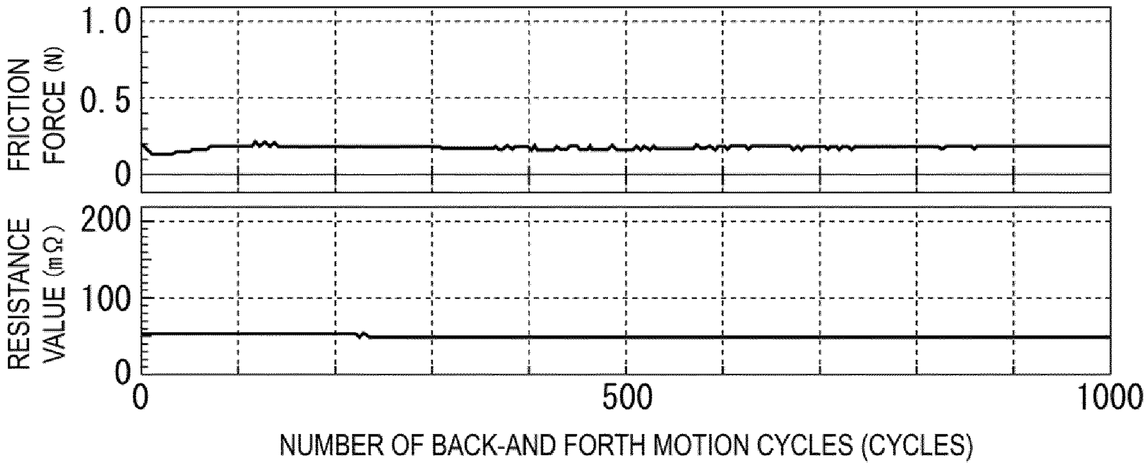
(a)

FIG. 3B



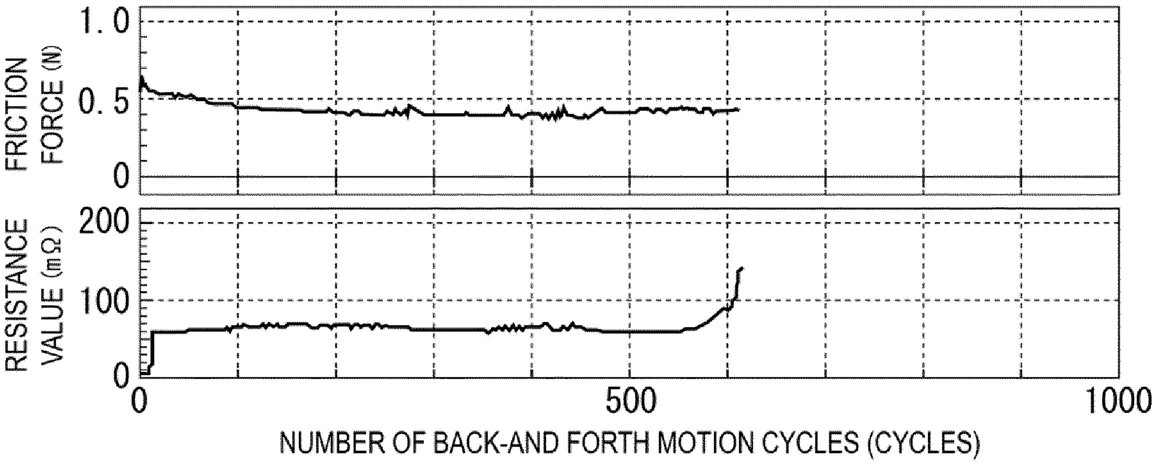
(b)

FIG. 4A



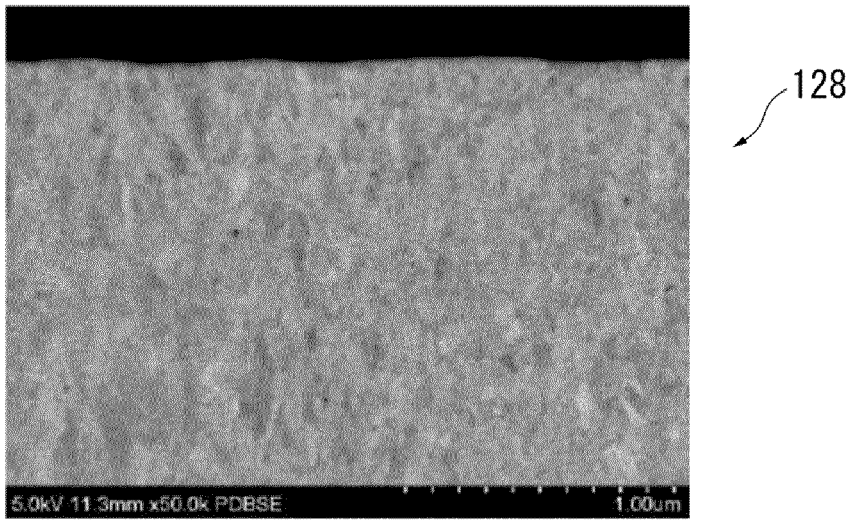
(a)

FIG. 4B



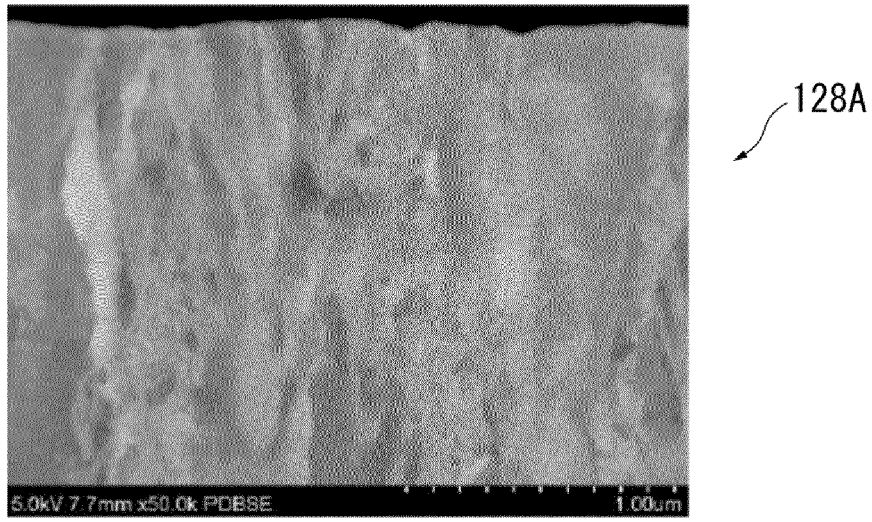
(b)

FIG. 5A



(a)

FIG. 5B



(b)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2018/046031

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl. C25D3/46(2006.01)i, C25D3/12(2006.01)i, C25D3/30(2006.01)i, C25D3/48(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. C25D3/46, C25D3/12, C25D3/30, C25D3/48

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	1971-2019
Registered utility model specifications of Japan	1996-2019
Published registered utility model applications of Japan	1994-2019

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 2013-185185 A (SHINSHU UNIVERSITY) 19 September 2013, claims, paragraphs [0001]-[0011], [0020]-[0035], fig. 5-12 (Family: none)	1, 3 2
Y	JP 2017-101301 A (TOYOTA MOTOR CORP.) 08 June 2017, claims, paragraphs [0001]-[0012], [0025]-[0039] (Family: none)	2

☐ 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
"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)
"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 13 February 2019 (13.02.2019)	Date of mailing of the international search report 26 February 2019 (26.02.2019)
Name and mailing address of the ISA/ Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan	Authorized officer Telephone No.

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 2008214667 A **[0004]**