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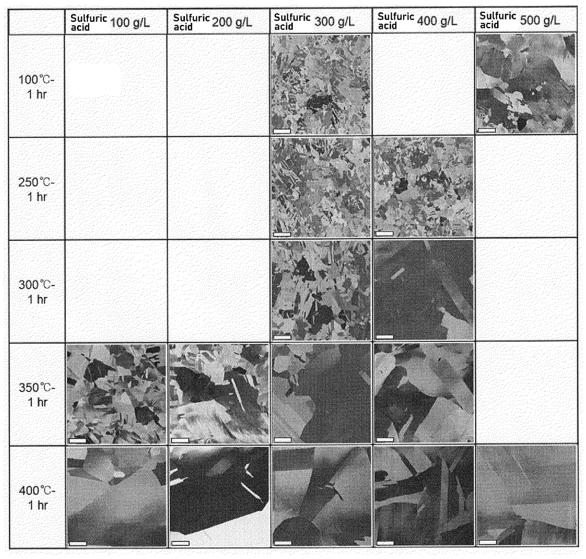
(54) METHOD FOR COARSENING COPPER CRYSTAL GRAINS IN OBJECTS TO BE PLATED AND COPPER-PLATED MEMBRANE HAVING COARSENED COPPER CRYSTAL GRAINS IN COPPER-PLATED MEMBRANE

(57) A copper-plated film having enlarged crystals can be obtained with a simple operation using a method for enlarging copper crystal grains in a plated object, the method including the following steps (a) and (b): (a) a step of electroplating an object to be plated in an electrolytic copper plating solution, which contains sulfuric acid, copper sulfate, chloride ions, a brightener, and a leveler, and in which the content of sulfuric acid is 200 g/L or more; and (b) a step of subjecting the electroplated object to be plated to a heat treatment at 400°C or lower.

FIG. 1



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Description

Technical Field

[0001] The present invention relates to a method for enlarging copper crystal grains in a plated object and a copper-plated film having enlarged copper crystal grains in the copper-plated film.

Background Art

[0002] In a circuit or the like made of a metal, non-uniform crystal grain size of the metal is undesirable because the electrical resistance increases. Therefore, it is desirable to uniformly enlarge crystal grains of a metal.

[0003] In order to enlarge crystal grains of a metal, it is necessary to hold the metal at a high temperature after completion of recrystallization. The driving force for grain growth is the grain boundary energy, and since the grain boundary area in a material is decreased by enlarging of the crystal grain size, the grain boundary energy corresponding to the decreased area serves as the driving force for grain growth.

[0004] However, unlike recrystallization, grain growth hardly occurs unless the temperature is relatively high (at least not lower than the half of the melting point), and in the case of copper, grain growth generally occurs at 1356 k / 2 = 678 k = 405°C or higher.

[0005] As a technique for enlarging crystal grains of copper, PTL 1 describes a method in which the concentration of chlorine in a compound containing chlorine and oxygen present as impurities at a crystal grain boundary is set to 2 atom% or less to reduce the intervention of impurities so that the crystal grain size in a copper wiring layer is increased to lower the resistivity and improve the electromigration resistance. In addition, PTL 2 describes a method in which uniform crystal grain enlarging is made possible by applying uniform strain due to plastic deformation through the steps of primary cold wire drawing, intermediate annealing, secondary cold wire drawing, and final annealing.

[0006] However, the above technique requires a plurality of delicate operations to enlarge copper crystals. Further, PTL 1 has a narrow application range because it is necessary to use high-purity raw materials, and there is a problem that it is difficult to adjust additives for expressing special performance such as filling performance and film thickness uniformity performance required for copper wiring formation for a semiconductor integrated circuit or a printed wiring board in addition to the performance unique to copper sulfate plating such as glossy appearance and ductility. Further, PTL 2 involves plastic deformation, and therefore there is a problem that it is difficult to apply to a semiconductor integrated circuit or a substrate.

Citation List

Patent Literature

[0007]

PTL 1: JP2014-222715A
PTL 2: JP4815878B

Summary of Invention

Technical Problem

[0008] Therefore, an object of the invention is to provide a technique capable of enlarging copper crystal grains with a simple operation.

Solution to Problem

[0009] The present inventors conducted intensive studies to achieve the above-mentioned object, and as a result, they found that by manipulating the concentration of sulfuric acid in a conventional copper sulfate plating solution, copper crystal grains can be easily enlarged at a heat treatment temperature lower than in the past, and thus completed the invention. In addition, the present inventors found that by the above operation, copper crystal grains in a copper-plated film obtained by copper plating are large, and a copper-plated film preferentially oriented along a specific crystal plane can be obtained, and thus completed the invention.

[0010] That is, the invention is directed to a method for enlarging copper crystal grains in a plated object, the method including the following steps (a) and (b):

(a) a step of electroplating an object to be plated in an electrolytic copper plating solution, which contains sulfuric acid, copper sulfate, chloride ions, a brightener, and a leveler, and in which the content of sulfuric acid is 200 g/L or more; and

(b) a step of subjecting the electroplated object to be plated to a heat treatment at 400°C or lower.

[0011] In addition, the invention is directed to a copper-plated film, in which copper crystal grains in the copper-plated film have a size of 5 um or more, and a crystal plane is preferentially oriented along (200) .

Advantageous Effects of Invention

[0012] The method for enlarging copper crystal grains in a plated object of the invention is a simple method of manipulating the concentration of sulfuric acid, and therefore is easy to implement.

[0013] In addition, the plated object having enlarged copper crystal grains in the plated object of the invention has a crystal plane preferentially oriented along (200), has a copper crystal grain size as large as 5 μm or more, and has a low electrical resistance, and therefore can be used for copper wiring, copper circuits, and the like.

[0014] Further, the plated object of the invention has a high thermal conductivity and can be used for a heat dissipation material of an electronic part.

Brief Description of Drawings

[0015]

[FIG. 1] FIG. 1 shows FIB-SIM images of a copper-plated film obtained in Example 1 (the magnification is 5000, which is the same in all images, and the scale bar in the drawing indicates 5 μm).

[FIG. 2] FIG. 2 shows the calculation results of the preferential orientation of a copper-plated film obtained with an electrolytic copper plating solution containing 50 g/L of copper sulfate, 300 g/L of sulfuric acid, and 40 g/L of chloride ions.

[FIG. 3] FIG. 3 shows FIB-SIM images of a copper-plated film obtained in Example 2 (the magnification is 5000, which is the same in all images, and the scale bar in the drawing indicates 5 μm).

[FIG. 4] FIG. 4 shows FIB-SIM images of a copper-plated film obtained in Example 3 (the magnification is 5000, which is the same in all images, and the scale bar in the drawing indicates 5 μm).

[FIG. 5] FIG. 5 shows an FIB-SIM image of a copper-plated film obtained in Example 4 (the magnification is 5000, and the scale bar in the drawing indicates 5 μm).

Description of Embodiments

[0016] The method for enlarging copper crystal grains in a plated object of the invention (hereinafter referred to as "the method of the invention") is a method including the following steps (a) and (b), preferably is a method in which the steps are performed in this order.

(a) a step of electroplating an object to be plated in an electrolytic copper plating solution, which contains sulfuric acid, copper sulfate, chloride ions, a brightener, and a leveler, and in which the content of sulfuric acid is 200 g/L or more

(b) a step of subjecting the electroplated object to be plated to a heat treatment at 400°C or lower

[0017] The object to be plated used in the step (a) of the method of the invention is not particularly limited as long as it can be plated with copper, and examples thereof include electronic parts such as a semiconductor integrated circuit and a printed wiring board, copper foil, a decorative material (a resin such as ABS, another metal, or the like), and a cooking utensil material such as a frying pan for thermal conductivity. Among these, an electronic part, copper foil, and the like are preferred.

[0018] The object to be plated may be subjected to, for example, a pretreatment such as washing, a moistening treatment, physical processing, a heat treatment, or rust prevention before the method of the invention is performed.

[0019] The electrolytic copper plating solution used in the step (a) of the method of the invention contains sulfuric acid, copper sulfate, chloride ions, a brightener, and a leveler. The lower limit of the content of sulfuric acid is 200 g/L or more, and preferably 250 g/L or more. The upper limit of the content of sulfuric acid is not particularly limited, but is preferably less than 500 g/L, more preferably 450 g/L or less, and particularly preferably 400 g/L or less. The range of the content of sulfuric acid in the electrolytic copper plating solution is 200 to less than 500 g/L, preferably 200 to 450 g/L, preferably 200 to 400 g/L, and preferably 250 to 400 g/L.

[0020] The concentration of copper sulfate in the electrolytic copper plating solution is not particularly limited, but is, for example, 10 to 300 g/L, and preferably 30 to 250 g/L when copper sulfate pentahydrate is used as the copper sulfate. When copper sulfate anhydride is used as the copper sulfate, the concentration may be calculated by conversion from the concentration of copper sulfate pentahydrate.

[0021] The concentration of chloride ions in the electrolytic copper plating solution is not particularly limited, but is, for example, 1 to 120 mg/L, and preferably 5 to 80 mg/L. A chloride ion source is not particularly limited, but examples thereof include hydrochloric acid and sodium chloride. Among these, hydrochloric acid is preferred.

[0022] The concentration of the brightener in the electrolytic copper plating solution is not particularly limited, but is, for example, 0.1 to 1,000 mg/L, and preferably 0.5 to 500 mg/L. The type of brightener is not particularly limited, but examples thereof include bis-(3-sodiumsulfopropyl) disulfide (SPS).

[0023] The concentration of the leveler in the electrolytic copper plating solution is not particularly limited, but is, for example, 0.1 to 10,000 mg/L, and preferably 1 to 1,000 mg/L. The type of leveler is not particularly limited, but for example, levelers such as a reaction product of a compound containing an amino group in the molecule and a compound containing an epoxy group in the molecule in the presence of an acid described in JP6782477B, preferably a reaction product described in Production Example 14, a reaction compound of a compound having three or more glycidyl ether groups and a heterocyclic compound described in JP5724068B, preferably a reaction compound described in Example 1, and a diallyldialkylammonium alkylsulfate-(meth)acrylamide-sulfur dioxide copolymer described in JP4895734B, preferably a diallyldialkylammonium alkylsulfate-(meth)acrylamide-sulfur dioxide copolymer described in Example 1 can be mentioned. Among these, a leveler described in JP6782477B is preferred.

[0024] Specifically, when a reaction product of a compound containing an amino group in the molecule and a compound containing an epoxy group in the molecule in the presence of an acid described in JP6782477B is used as the leveler, crystal grains can be enlarged at a sulfuric acid concentration of 200 to 450 g/L and a heat treatment temperature of 300 to 350°C.

[0025] In addition, when a reaction compound of a compound having three or more glycidyl ether groups and a heterocyclic compound described in JP5724068B or a diallyldialkylammonium alkylsulfate-(meth)acrylamide-sulfur dioxide copolymer described in JP4895734B is used as the leveler, copper crystal grains can be enlarged at a sulfuric acid concentration of 400 to 450 g/L and a heat treatment temperature of 350 to 400°C.

[0026] In addition to the leveler and the brightener, the electrolytic copper plating solution may further contain a carrier. The concentration of the carrier is not particularly limited, but is, for example, 0.1 to 10,000 mg/L, and preferably 1 to 1,000 mg/L. The type of carrier is not particularly limited, and examples thereof include polyethylene glycols (molecular weight: 100 to 20,000). Among these, a polyethylene glycol (molecular weight: 2,000 to 10,000) is preferred.

[0027] Plating conditions in the method of the invention are not particularly limited, and electricity in a range of 0.1 to 30 A/dm^2 is applied to deposit copper on the object to be plated while the solution is stirred by air stirring, jet stirring, paddle stirring, or the like using the plating solution, a plating tank equipped with piping for air stirring, piping for jet stirring, a stirring blade or the like, a phosphorus-containing copper anode or an insoluble anode, and a DC power supply.

[0028] After the object to be plated is electroplated in the step (a) of the method of the invention, for example, a treatment such as rust prevention or physical processing may be performed.

[0029] In the step (b) of the method of the invention, the electroplated object to be plated is subjected to a heat treatment at 400°C or lower. The heating temperature is preferably 300°C or higher, more preferably 300°C or higher and 400°C or lower, and particularly preferably 300 to 350°C. Further, the heating time is not particularly limited, but is, for example, 1 to 180 minutes, and preferably 10 to 120 minutes. This heat treatment is not particularly limited, and examples thereof include a heat treatment using a step of thermocompression bonding a resin material and copper foil or the like in a step of producing a printed wiring board, a heat treatment using a solder reflow step, a heat treatment using CVD, PVD, or copper bonding of a CMOS sensor or the like in a step of producing a semiconductor integrated circuit, and a heat treatment using an electric furnace.

[0030] According to the method of the invention described above, a plated object having enlarged copper crystal grains in the copper-plated film is obtained. Here, the enlarged copper crystal grains in the plated object means that the crystal grain size is 5 um or more. That is, in the stabilization of copper crystal grains that occur near room temperature, the size is 5 μm or less, and in the method of the invention, a plated object having a copper crystal grain size of 5 μm or more is obtained. Further, this can be checked by obtaining an SIM image of a sample subjected to FIB (focused ion beam) processing.

[0031] In the obtained copper-plated film, copper crystal grains have a size of 5 um or more, and preferably 5 to 100 um, and the crystal plane has a preferential orientation along (200), more preferably 90% or more of which is oriented along (200). Further, the plated object has a maximum stress of 5 to 15 kgf/mm^2 and a hardness of 30 to 70 HV.

[0032] The expression "copper crystal grains have a size of 5 um or more" refers to, for example, a copper crystal grain with one side of the crystal grain boundary being clearly 5 um or more in a copper crystal grain of a copper-plated film observed by FIB-SIM observation. The orientation of the crystal plane was determined by calculation using the Wilson equation from the results of X-ray diffraction obtained by an X-ray diffractometer (Koichiro Inoue et al., "Surface

Morphology and Orientation of Electrodeposited Fe Films", Journal of the Japan Institute of Metals and Materials, Vol. 65, No. 4 (2001) 229-235). The expression "the crystal plane has a preferential orientation along (200)" means that one having the highest orientation coefficient among values greater than 1 calculated by the Wilson equation is referred to as a preferential orientation plane (preferential orientation). Further, the expression "90% or more of which is oriented along (200)" means that the proportion of preferential orientation in the orientation coefficient is 90% or more of all the orientation coefficients. The maximum stress is a value measured with a tensile tester (precision universal tester). The hardness is a value measured with a Vickers hardness meter.

[0033] The plated object of the invention has enlarged copper crystal grains in the plated object, and therefore can be used for wiring, circuits, heat dissipation materials, and the like

Examples

[0034] Hereinafter, the invention will be described in detail with reference to Examples, but the invention is by no means limited to these Examples.

Example 1

[0035] Enlarging of Copper Crystal Grains:
Stainless steel (SUS 304) was subjected to electrolytic copper plating (film thickness: 60 um) under the conditions of a current density of 1.5 A/dm^2 and a plating time of 180 minutes by changing the concentration of sulfuric acid in a range of 100 g/L to 500 g/L in an electrolytic copper plating solution having the following basic composition. Subsequently, the copper-plated film is peeled off from the stainless steel (SUS 304). The peeled copper-plated film was placed in a heating furnace and subjected to a heat treatment in a range of 100°C to 400°C in an inert gas (nitrogen) atmosphere for 60 minutes. The copper-plated film after the heat treatment was observed with an FIB-SIM (Hitachi High-Tech Corporation: FB-2100). The results are shown in FIG. 1. In addition, the copper-plated film after the heat treatment was analyzed with an X-ray diffractometer (Shimadzu Corporation: XRD-6100), and the preferential orientation of the crystal plane was calculated by the Wilson equation (as an example of the results, the calculation results of the copper-plated film after the heat treatment obtained with an electrolytic copper plating solution containing 50 g/L of copper sulfate, 300 g/L of sulfuric acid, and 40 g/L of chloride ions are shown in FIG. 2).

<Basic Composition of Electrolytic Copper Plating Solution>

[0036]

- Sulfuric acid: 100 g/L to 500 g/L
- Copper sulfate pentahydrate: 50 g/L
- Chloride ions: 40 mg/L
- Carrier: 0.5 g/L of PEG 10000
- Brightener: 10 mg/L of SPS
- Leveler: 100 mg/L of the leveler described in Production Example 14 in JP6782477B

[0037] (The preparation method is according to the method described in the same description.)

<X-ray Diffraction Conditions>

[0038]

X-ray source: CuKα ray
X-ray voltage: 40 kV
X-ray current: 30 mA
Diffraction angle: 40 to 150°
Measurement speed: 2°/min
Test piece size: 50 × 50 mm
Copper film thickness: 60 μm

[0039] From the results, enlarging of crystal grains occurred at 400°C in the case of 100 g/L of sulfuric acid, at 350°C in the case of 200 g/L and 300 g/L of sulfuric acid, and at 300°C in the case of 400 g/L of sulfuric acid. On the other hand, a semi-glossy appearance was obtained in the case of 500 g/L, and coarse crystal grains were formed immediately after deposition, and a different tendency from the enlarging of crystal grains by a heat treatment was exhibited. From the FIB-SIM observation, it was found that the enlarged copper crystal grains have a crystal grain size of 5 um or more with one side of the crystal grain boundary being clearly 5 um or more. It was also found that the crystal planes of the enlarged copper crystal grains are preferentially oriented along the (200) plane.

Example 2

[0040] Enlarging of Copper Crystal Grains:
Stainless steel (SUS 304) was subjected to electrolytic copper plating (film thickness: 60 um) under the conditions of a current density of 1.5 A/dm^2 and a plating time of 180 minutes by changing the concentration of copper sulfate pentahydrate in a range of 50 g/L to 200 g/L in an electrolytic copper plating solution having the following basic composition. Subsequently, the copper-plated film is peeled off from the stainless steel (SUS 304). The peeled copper-plated film was placed in a heating furnace and subjected to a heat treatment in a range of 100°C to 400°C in an inert gas (nitrogen) atmosphere for 60 minutes. The copper-plated film after the heat treatment was observed with an FIB-SIM. The results are shown in FIG. 3. In addition, with respect to the copper-plated film after the heat treatment, the preferential orientation of the crystal plane was calculated in the same manner as in Example 1.

<Basic Composition of Electrolytic Copper Plating Solution>

[0041]

- · Sulfuric acid: 200 g/L
- · Copper sulfate pentahydrate: 50 to 200 g/L
- · Chloride ions: 40 mg/L
- · Carrier: 0.5 g/L of PEG 10000
- · Brightener: 10 mg/L of SPS
- · Leveler: 100 mg/L of the leveler described in Production Example 14 in JP6782477B

[0042] (The preparation method is according to the method described in the same description.)

[0043] From the results, enlarging of crystal grains occurred at 400°C under all conditions. This showed that the enlarging of crystal grains occurs not due to the concentration of copper sulfate but due to the concentration of sulfuric acid in the plating solution of the invention. From the FIB-SIM observation, it was found that the enlarged copper crystal grains have a crystal grain size of 5 um or more with one side of the crystal grain boundary being clearly 5 um or more. It was also found that the crystal planes of the enlarged copper crystal grains are preferentially oriented along the (200) plane.

Example 3

[0044] Enlarging of Copper Crystal Grains:
Stainless steel (SUS 304) was subjected to electrolytic copper plating (film thickness: 60 um) under the conditions of a current density of 1.5 A/dm^2 and a plating time of 180 minutes using each of levelers A to C in an electrolytic copper plating solution having the following basic composition. Subsequently, the copper-plated film is peeled off from the stainless steel (SUS 304). The peeled copper-plated film was placed in a heating furnace and subjected to a heat treatment at a predetermined temperature in an inert gas (nitrogen) atmosphere for 60 minutes. The copper-plated film after the heat treatment was observed with an FIB-SIM. The results are shown in FIG. 4. In addition, with respect to the copper-plated film after the heat treatment, the preferential orientation of the crystal plane was calculated in the same manner as in Example 1.

<Basic Composition of Electrolytic Copper Plating Solution>

[0045]

- · Sulfuric acid: 400 g/L
- · Copper sulfate pentahydrate: 50 g/L
- · Chloride ions: 40 mg/L
- · Carrier: 0.5 g/L of PEG 10000
- · Brightener: 10 mg/L of SPS

<Leveler>

[0046]

- Leveler A: 100 mg/L of the leveler described in Production Example 14 in JP6782477B
(The preparation method is according to the method described in the same description.)
- Leveler B: 100 mg/L of the leveler described in Example 1 in JP5724068B
(The preparation method is according to the method described in the same description.)
- Leveler C: 100 mg/L of the leveler described in Example 1 in JP4895734B
(The preparation method is according to the method described in the same description.)

[0047] From the results, it was found that the crystal grains are enlarged by a heat treatment at 400°C or lower with all the levelers used in Example 3. From the FIB-SIM observation, it was found that the enlarged copper crystal grains have a crystal grain size of 5 um or more with one side of the crystal grain boundary being clearly 5 um or more. It was also found that the crystal planes of the enlarged copper crystal grains are preferentially oriented along the (200) plane.

[0048] Further, it was found that the enlarging of copper crystal grains occurs by a heat treatment at 300°C or higher in the case of using the leveler A, the leveler B, and the leveler C with 400 g/L of sulfuric acid.

Example 4

[0049] Enlarging of Copper Crystal Grains:
A material obtained by forming a thermal oxide film on a silicon single crystal, and then depositing titanium to a thickness of 100 nm and copper to a thickness of 400 nm through sputtering was subjected to electrolytic copper plating (film thickness: 5 um) under the conditions of a current density of 1.0 A/dm^2 and a plating time of 22.5 minutes in an electrolytic copper plating solution having the following basic composition. Subsequently, the plated object was placed in a heating furnace and subjected to a heat treatment at 350°C in an inert gas (nitrogen) atmosphere for 60 minutes. The plated object after the heat treatment was observed with an FIB-SIM. The result is shown in FIG. 5. In addition, with respect to the plated object after the heat treatment, the preferential orientation of the crystal plane was calculated in the same manner as in Example 1.

<Basic Composition of Electrolytic Copper Plating Solution>

[0050]

- Sulfuric acid: 400 g/L
- Copper sulfate pentahydrate: 50 g/L
- Chloride ions: 40 mg/L
- Carrier: 0.5 g/L of PEG 10000
- Brightener: 10 mg/L of SPS
- Leveler: 100 mg/L of the leveler described in Production Example 14 in JP6782477B

[0051] (The preparation method is according to the method described in the same description.)

[0052] From the results, it was found that enlarging of copper crystal grains in the plated object occurs by a heat treatment at 400°C or lower on a material on which copper was deposited by sputtering used in Example 4. From the FIB-SIM observation, it was found that the enlarged copper crystal grains have a crystal grain size of 5 um or more with one side of the crystal grain boundary being clearly 5 um or more. It was also found that the crystal planes of the enlarged copper crystal grains are preferentially oriented along the (200) plane.

Test example 1

[0053] Measurement of Physical Properties:
With respect to the copper-plated film after the heat treatment (100°C, 300°C, or 350°C) obtained with the electrolytic copper plating solution containing 50 g/L of copper sulfate, 300 g/L of sulfuric acid, and 40 g/L of chloride ions in Example 1, a stress (tensile test method) and a hardness were measured. The results are shown in Tables 1 and 2.

<Stress Measurement Conditions>

[0054]

Precision universal tester: Autograph AGS-X, 10N-10kN (Shimadzu Corporation)
Tensile speed: 10 mm/min
Tensile load: 50 kgf/Full Scale
Heat treatment: 120°C, 60 min
in accordance with JIS standard: Z-2241 (1980)
Test piece: in accordance with JIS standard: K-7162-1B

<Hardness Measurement Conditions>

[0055]

Vickers hardness tester: HM-200 (Mitutoyo)
Test force: 0.01 kgf
Loading time: 4 sec
Holding time: 15 sec
Unloading time: 4 sec
Approaching speed: 60 μm/sec
Test piece size: 40 × 15 mm
Copper film thickness: 60 μm
JIS standard: Z-2244 (2009)

[Table 1]

Heat treatment temperature	Crystal grain size	Sample name	Thickness	Width	Gauge length	Test force	Stress
°C	μm	No.	mm	mm	mm	kgf	kgf/mm^2
100	2 or less	1	0.058	10	50	18.6	32.1
		2	0.058	10	50	19.0	32..8
		3	0.058	10	50	18.7	32.2
		average	0.058	10	50	18.8	32.4
300	2 to 5	1	0.058	10	50	9.8	16.9
		2	0.058	10	50	10.2	17.5
		3	0.058	10	50	10.0	17.3
		average	0.058	10	50	10.0	17.3
350	5 or more	1	0.058	10	50	5.8	9.9
		2	0.058	10	50	5.7	9.8
		3	0.058	10	50	6.0	10.4
		average	0.058	10	50	5.8	10.0
400	5 or more	1	0.058	10	50	5.7	9.8
		2	0.058	10	50	5.7	9.8
		3	0.058	10	50	5.9	10.2
		average	0.058	10	50	5.8	9.9

[Table 2]

Heat treatment temperature	Crystal grain size	Sample name	Thickness	Hardness
°C	μm	No.	mm	HV

(continued)

Heat treatment temperature	Crystal grain size	Sample name	Thickness	Hardness
100	2 or less	1	0.058	111.0
		2	0.058	101.0
		3	0.058	111.0
		average	0.058	107.7
300	2 to 5	1	0.058	78.2
		2	0.058	62.6
		3	0.058	70.5
		average	0.058	70.4
350	5 or more	1	0.058	52.7
		2	0.058	49.7
		3	0.058	52.7
		average	0.058	51.7
400	5 or more	1	0.058	50.5
		2	0.058	51.7
		3	0.058	49.3
		average	0.058	50.5

[0056] From the above results, the stress was 5 to 15 kgf/mm^2 and the hardness was 30 to 70 HV when the copper crystal grain size was 5 μm or more and the crystal plane was preferentially oriented along (200).

Industrial Applicability

[0057] The method for enlarging copper crystal grains in a plated object and a plated object having enlarged copper crystal grains in the plated object of the invention can be used for wiring, circuits, heat dissipation materials, and the like.

Claims

1. A method for enlarging copper crystal grains in a plated object, the method comprising the following steps (a) and (b):

   (a) a step of electroplating an object to be plated in an electrolytic copper plating solution, which contains sulfuric acid, copper sulfate, chloride ions, a brightener, and a leveler, and in which the content of sulfuric acid is 200 g/L or more; and
   (b) a step of subjecting the electroplated object to be plated to a heat treatment at 400°C or lower.

2. The method for enlarging copper crystal grains in a plated object according to claim 1, wherein the heat treatment in the step (b) is at 300°C or higher.

3. The method for enlarging copper crystal grains in a plated object according to claim 1 or 2, wherein the content of sulfuric acid in the step (a) is less than 500 g/L.

4. A copper-plated film, wherein copper crystal grains in the copper-plated film have a size of 5 um or more, and a crystal plane is preferentially oriented along (200).

FIG. 1

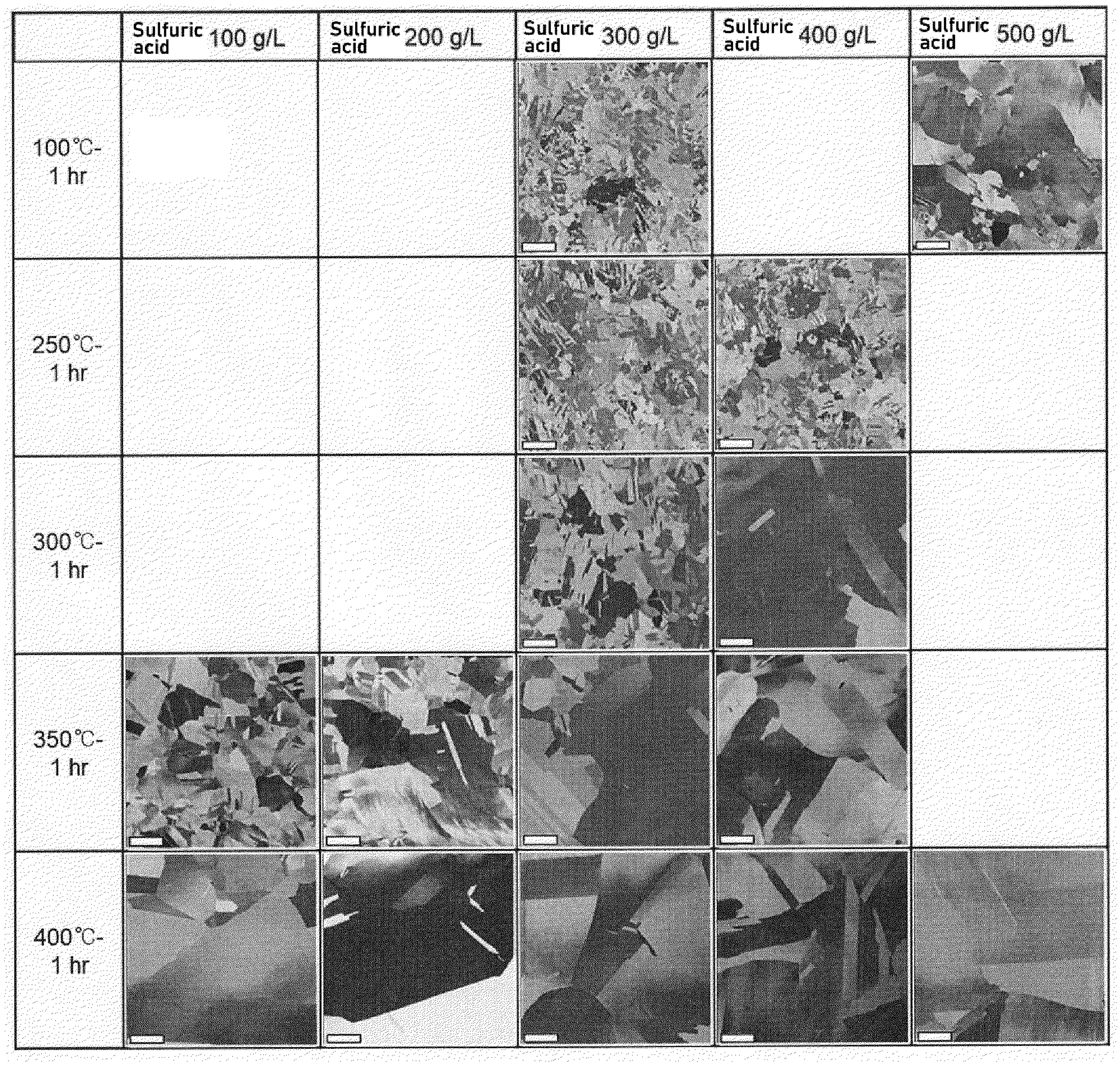

Sulfuric acid 100 g/L
Sulfuric acid 200 g/L
Sulfuric acid 300 g/L
Sulfuric acid 400 g/L
Sulfuric acid 500 g/L
100℃-1 hr
250℃-1 hr
300℃-1 hr
350℃-1 hr
400℃-1 hr

FIG. 2

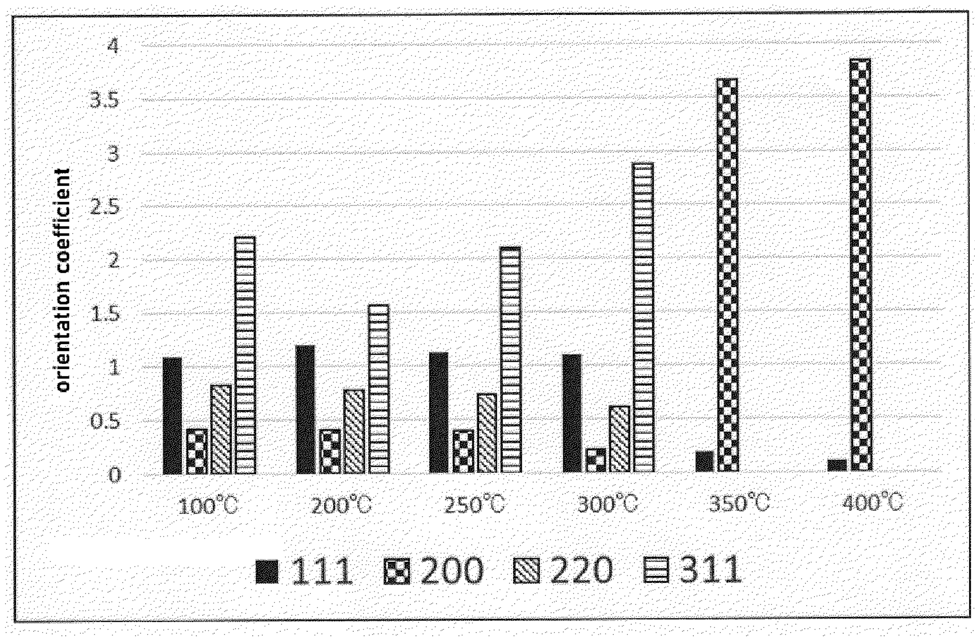

orientation coefficient
4
3.5
3
2.5
2
1.5
1
0.5
0
100℃
200℃
250℃
300℃
350℃
400℃
■ 111
▩ 200
▨ 220
▤ 311

FIG. 3

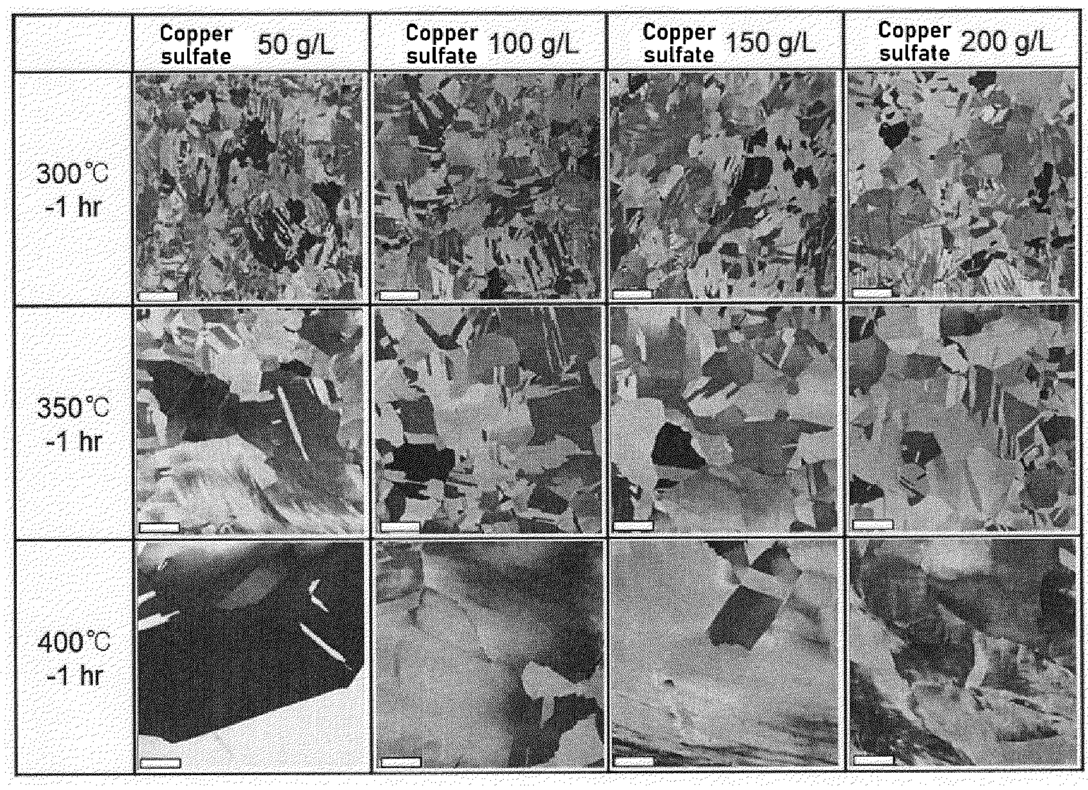

Copper sulfate 50 g/L
Copper sulfate 100 g/L
Copper sulfate 150 g/L
Copper sulfate 200 g/L
300℃ -1 hr
350℃ -1 hr
400℃ -1 hr

FIG. 4

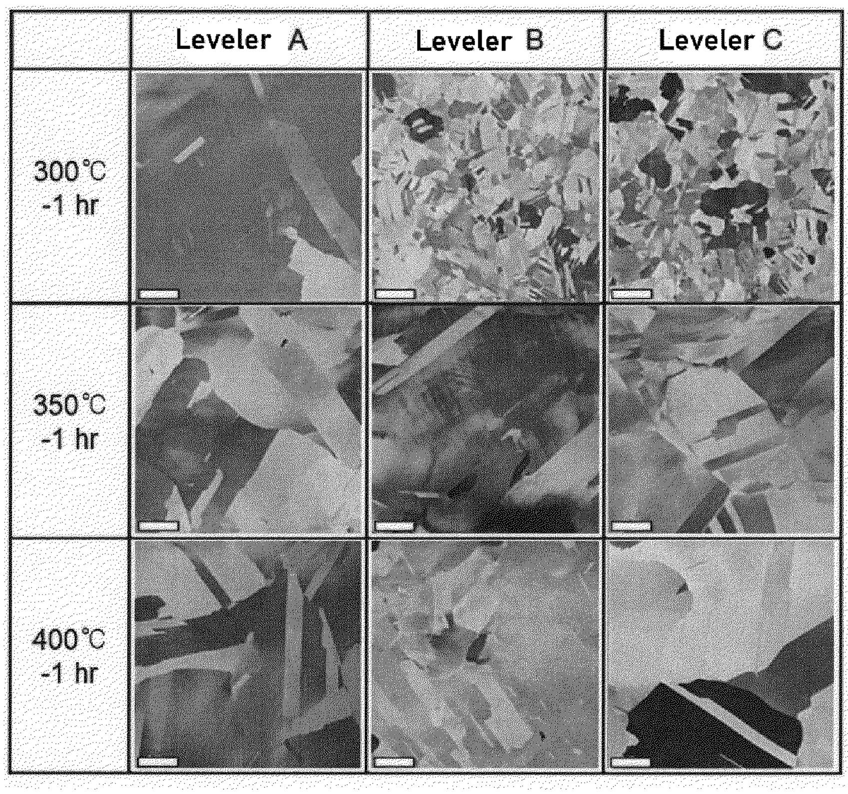
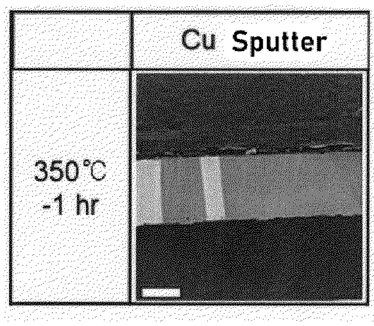

Leveler A
Leveler B
Leveler C
300℃ -1 hr
350℃ -1 hr
400℃ -1 hr

FIG. 5


Cu Sputter
350℃ -1 hr

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2022/035799

A. CLASSIFICATION OF SUBJECT MATTER

C25D 5/50(2006.01)i; ***C25D 1/00***(2006.01)i; ***C25D 1/04***(2006.01)i; ***C25D 3/38***(2006.01)i
FI: C25D5/50; C25D1/04 311; C25D3/38 101; C25D1/00 311

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)

C25D5/50; C25D1/00; C25D1/04; C25D3/38

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 1971-2022
Registered utility model specifications of Japan 1996-2022
Published registered utility model applications of Japan 1994-2022

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.
A	JP 2008-88524 A (EBARA UDYLITE KK) 17 April 2008 (2008-04-17) entire text	1-4
A	JP 7-102392 A (SUMITOMO METAL MINING CO., LTD.) 18 April 1995 (1995-04-18) entire text	1-4
A	JP 2012-127003 A (ROHM & HAAS ELECTRONIC MATERIALS LLC) 05 July 2012 (2012-07-05) entire text	1-4
A	JP 2014-222715 A (IBARAKI UNIVERSITY) 27 November 2014 (2014-11-27) entire text	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
"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 **12 December 2022**	Date of mailing of the international search report **20 December 2022**
Name and mailing address of the ISA/JP **Japan Patent Office (ISA/JP)** **3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915** **Japan**	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/JP2022/035799

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
JP 2008-88524 A	17 April 2008	(Family: none)	
JP 7-102392 A	18 April 1995	(Family: none)	
JP 2012-127003 A	05 July 2012	US 2012/0318676 A1 EP 2465976 A1 CN 102534702 A KR 10-2012-0067315 A TW 201231736 A	
JP 2014-222715 A	27 November 2014	WO 2014/185187 A1	

Form PCT/ISA/210 (patent family annex) (January 2015)

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- JP 4815878 B **[0007]**
- JP 6782477 B **[0023] [0024] [0036] [0041] [0046] [0050]**
- JP 5724068 B **[0023] [0025] [0046]**
- JP 4895734 B **[0023] [0025] [0046]**

Non-patent literature cited in the description

- **KOICHIRO INOUE et al.** Surface Morphology and Orientation of Electrodeposited Fe Films. *Journal of the Japan Institute of Metals and Materials,* 2001, vol. 65 (4), 229-235 **[0032]**