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(54) **METHOD FOR PRODUCING METAL THIN BODY**

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(57) **ABSTRACT**

A method for producing a metal thin body by electroplating, in which the relative integrated intensity of the (111) plane of the metal thin body can be increased to 65% or greater. By carrying out electroplating using an electrolytic solution (plating solution) containing 5% in volume or greater of acetonitrile and water, in particular, using an electrolytic solution (plating solution) containing 10% in volume or greater of acetonitrile and water, the relative integrated intensity of the (111) plane can be increased to 65% or greater.

32 %-CH$_3$CN

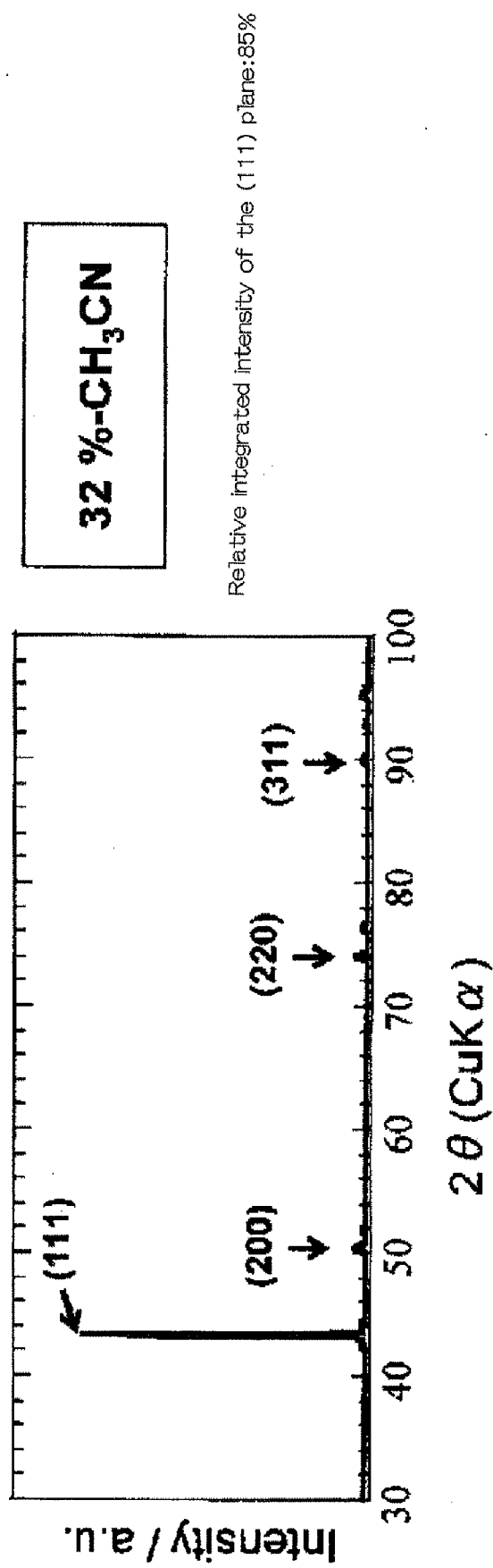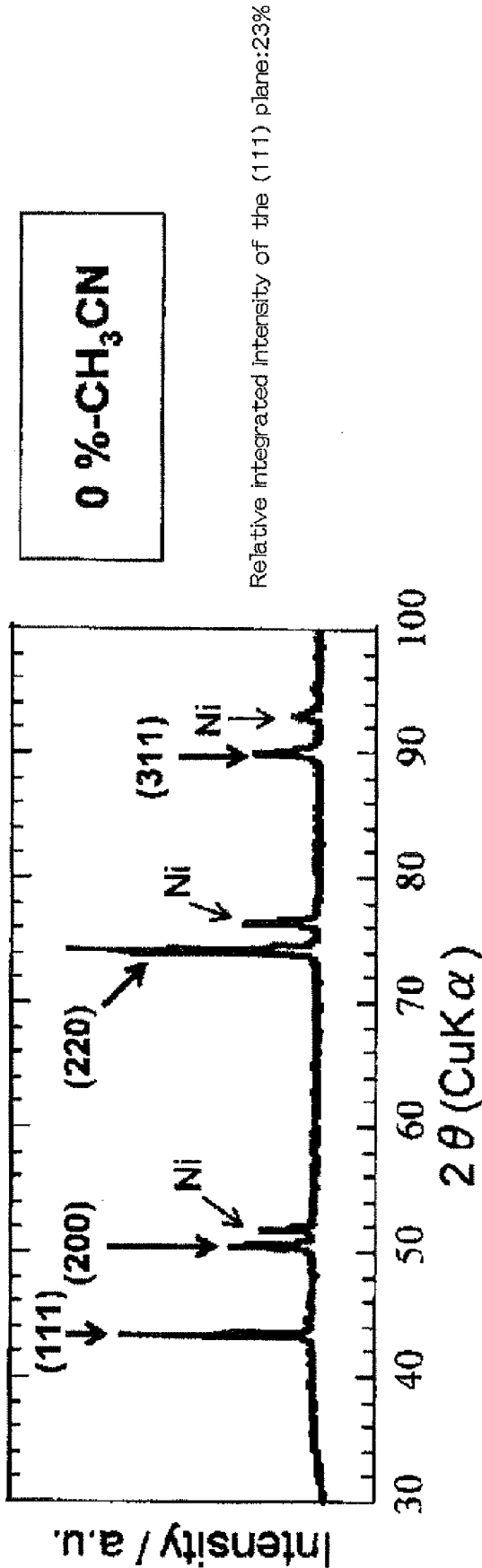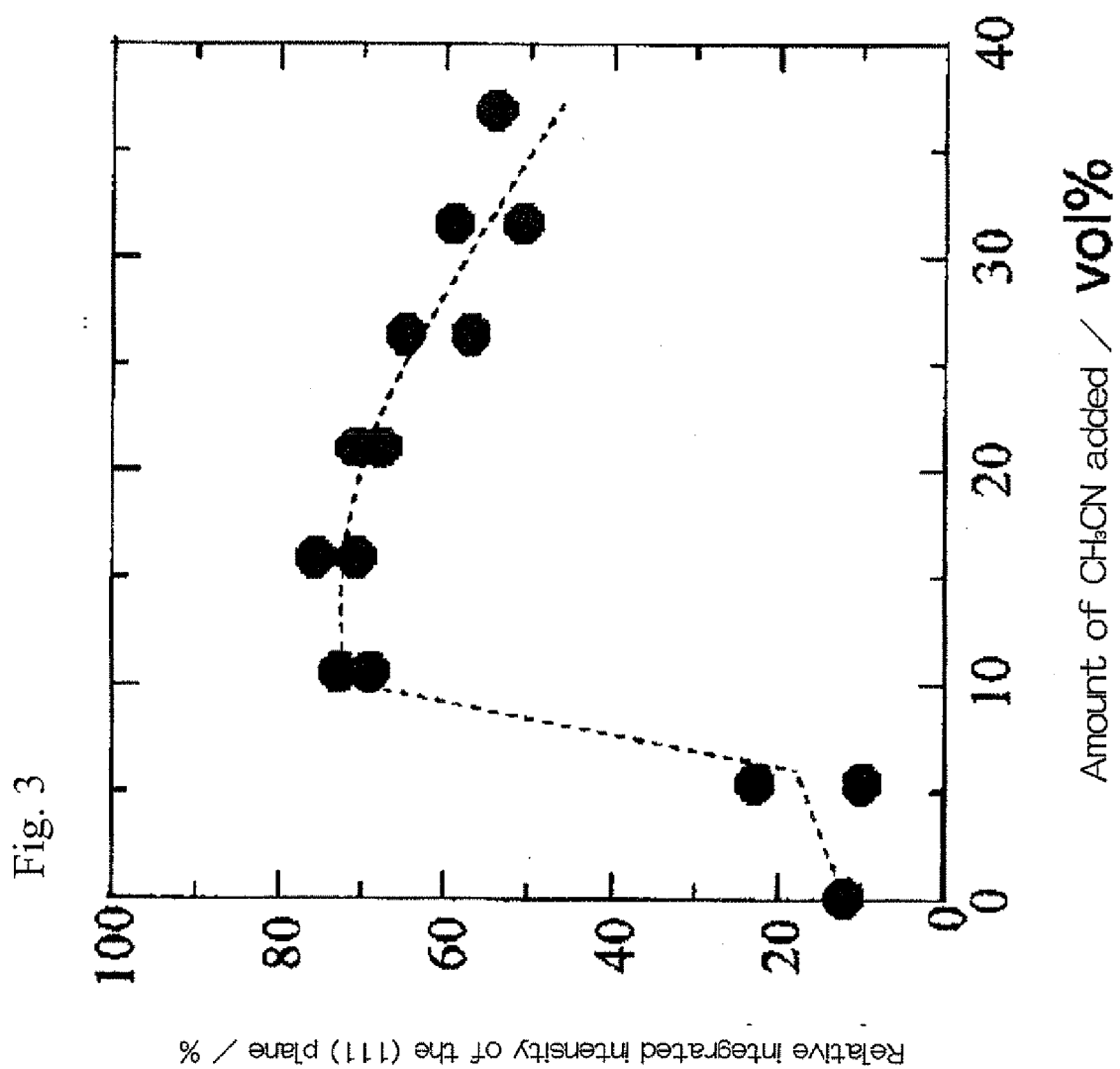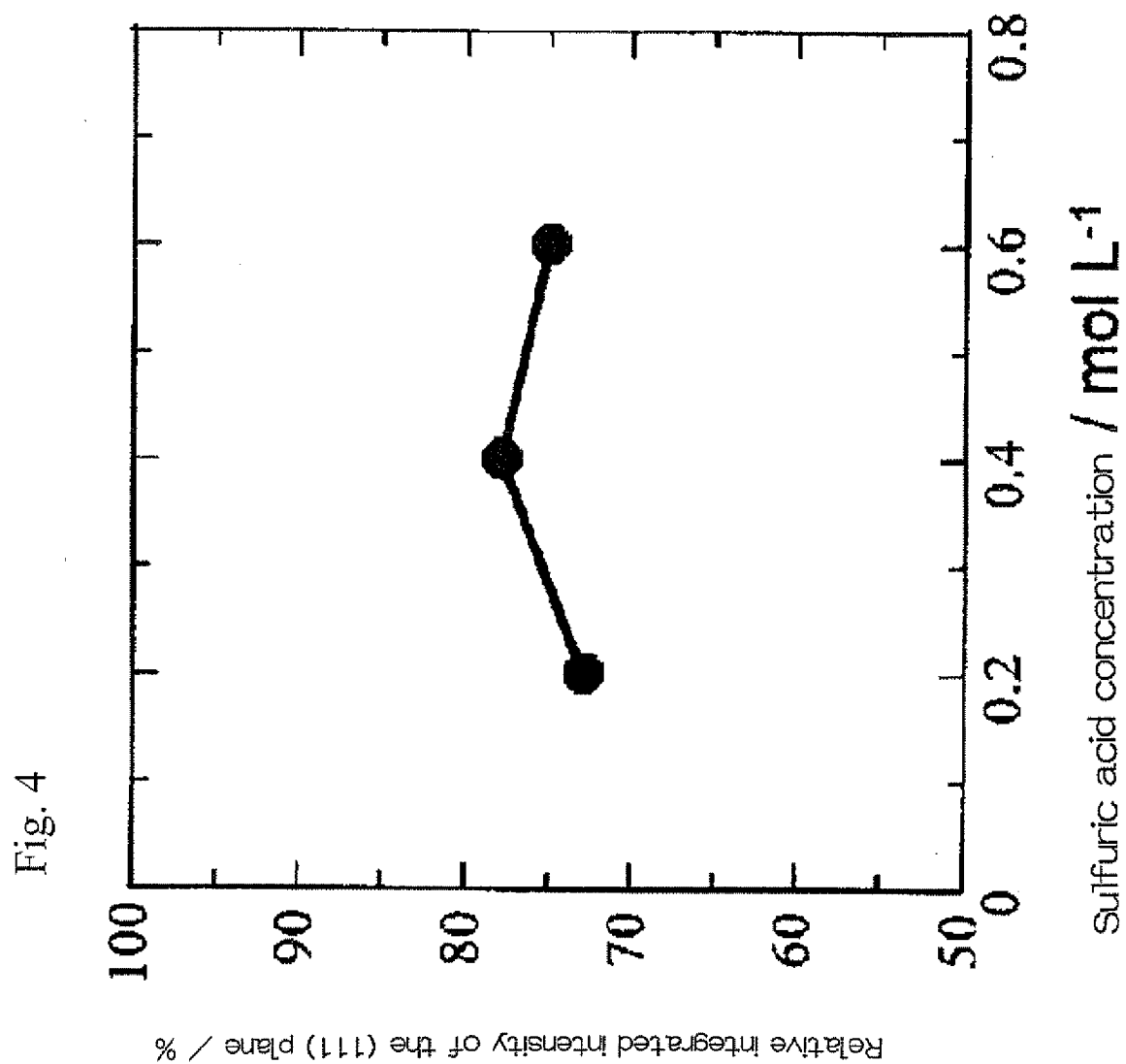Relative integrated intensity of the (111) plane:85%

Fig. 1

Fig. 2

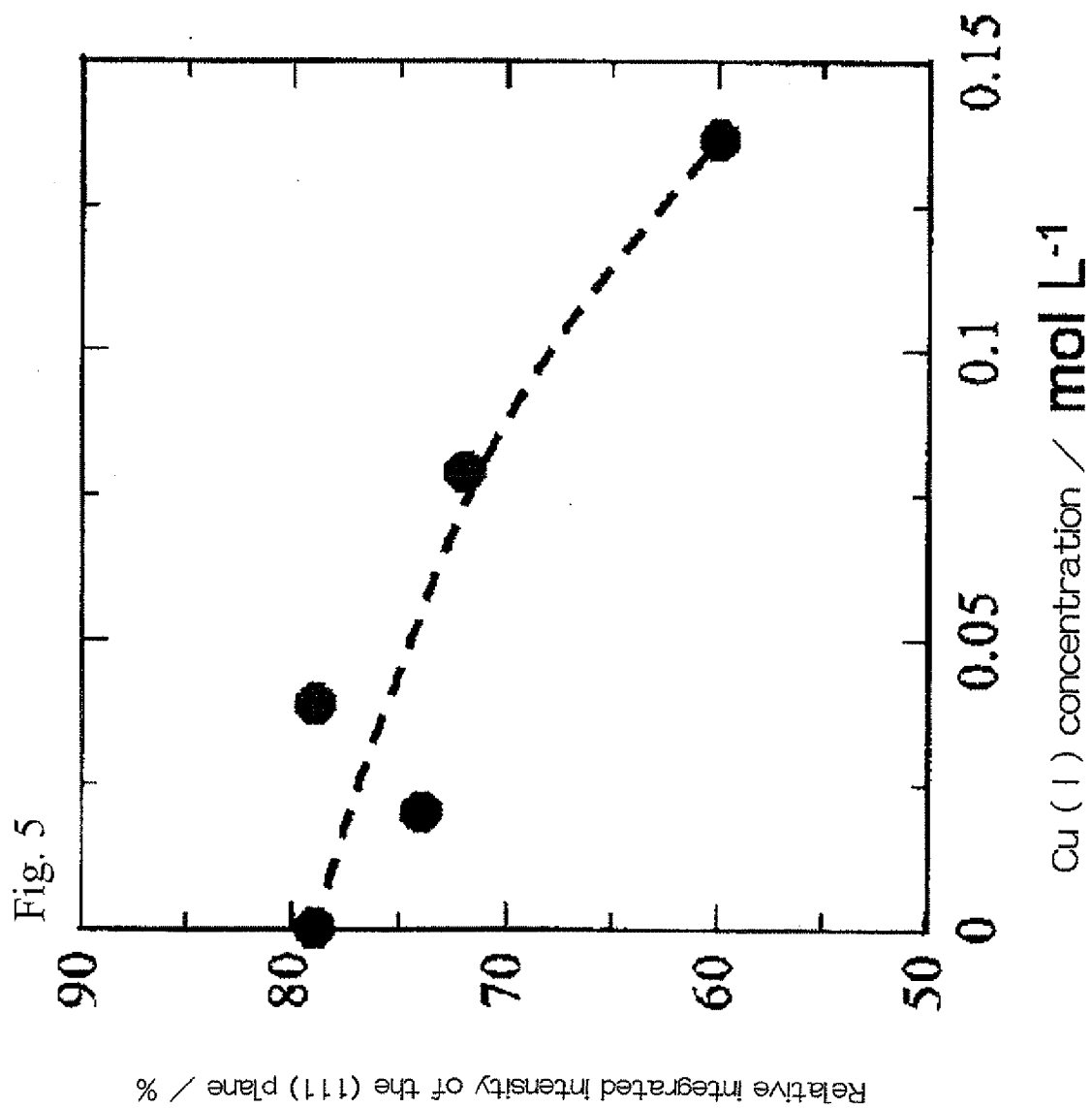0 %-CH₃CN

Relative integrated intensity of the (111) plane:23%

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

METHOD FOR PRODUCING METAL THIN BODY

TECHNICAL FIELD

[0001] The present invention relates to methods for producing a metal thin body including a metal film, a metal foil, or a tape, a sheet and the like; it relates specifically to methods for producing a metal thin body by electroplating, and among of them, in particular, methods for producing a copper thin body.

BACKGROUND ART

[0002] Various methods are known for the preparation of a metal thin body, such as, PVD methods such as non-electrolytic plating, vacuum deposition and sputtering, in addition to electroplating (also referred to as electrolytic plating and electrodeposition method). Among these, electroplating has advantages such as, products can be obtained with a wide range of thickness from thin to relatively thick by adjusting the electrolysis time (electrical transmission time), in addition, the amount of hydrogen generated is small compared to non-electrolytic plating or the like, and being a low temperature process carried out at room temperature to around 50° C., deposit formation is possible on a substrate having low resistance to heat. In addition, with the development of the damascene method (wiring process combining copper sulf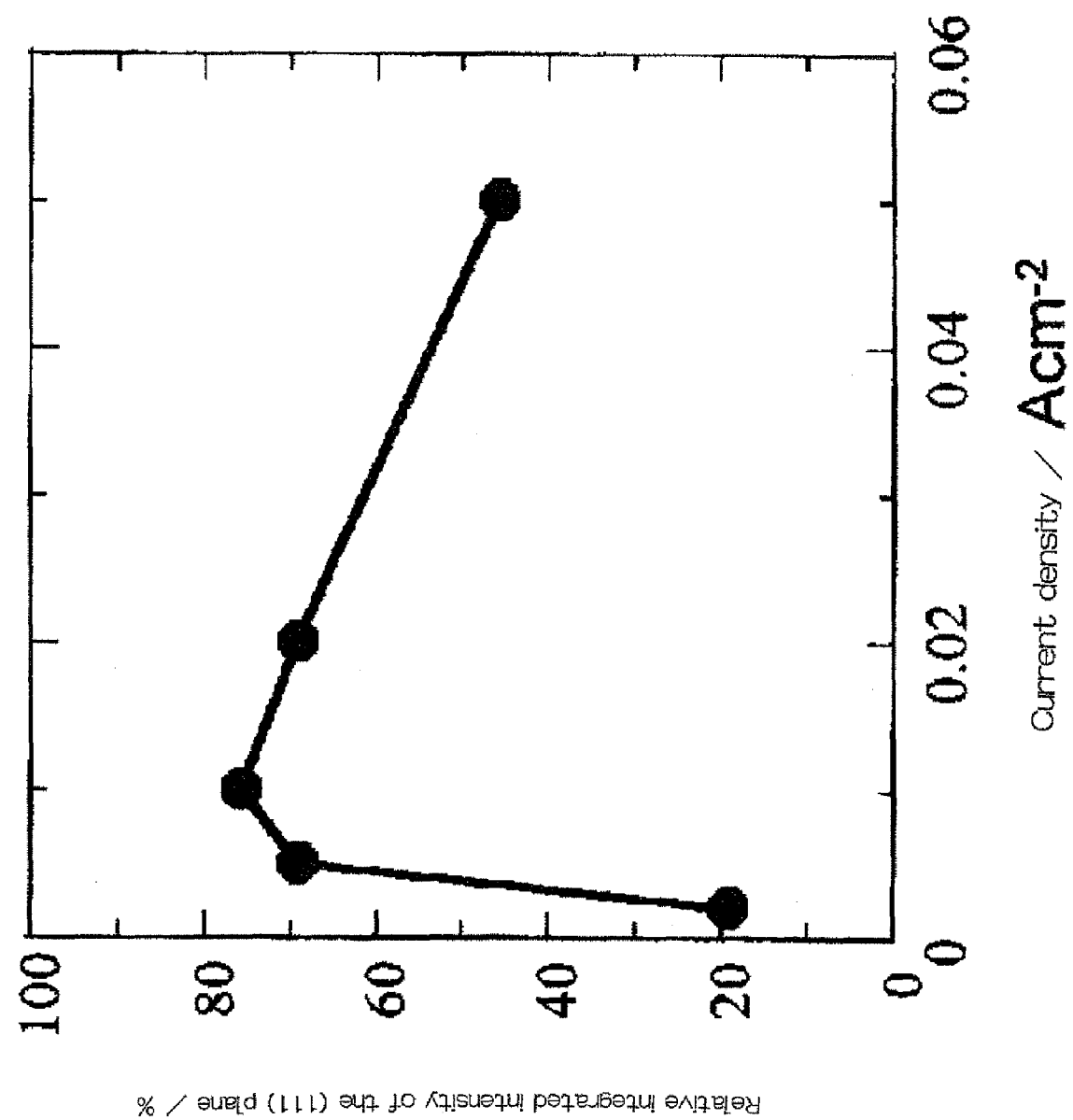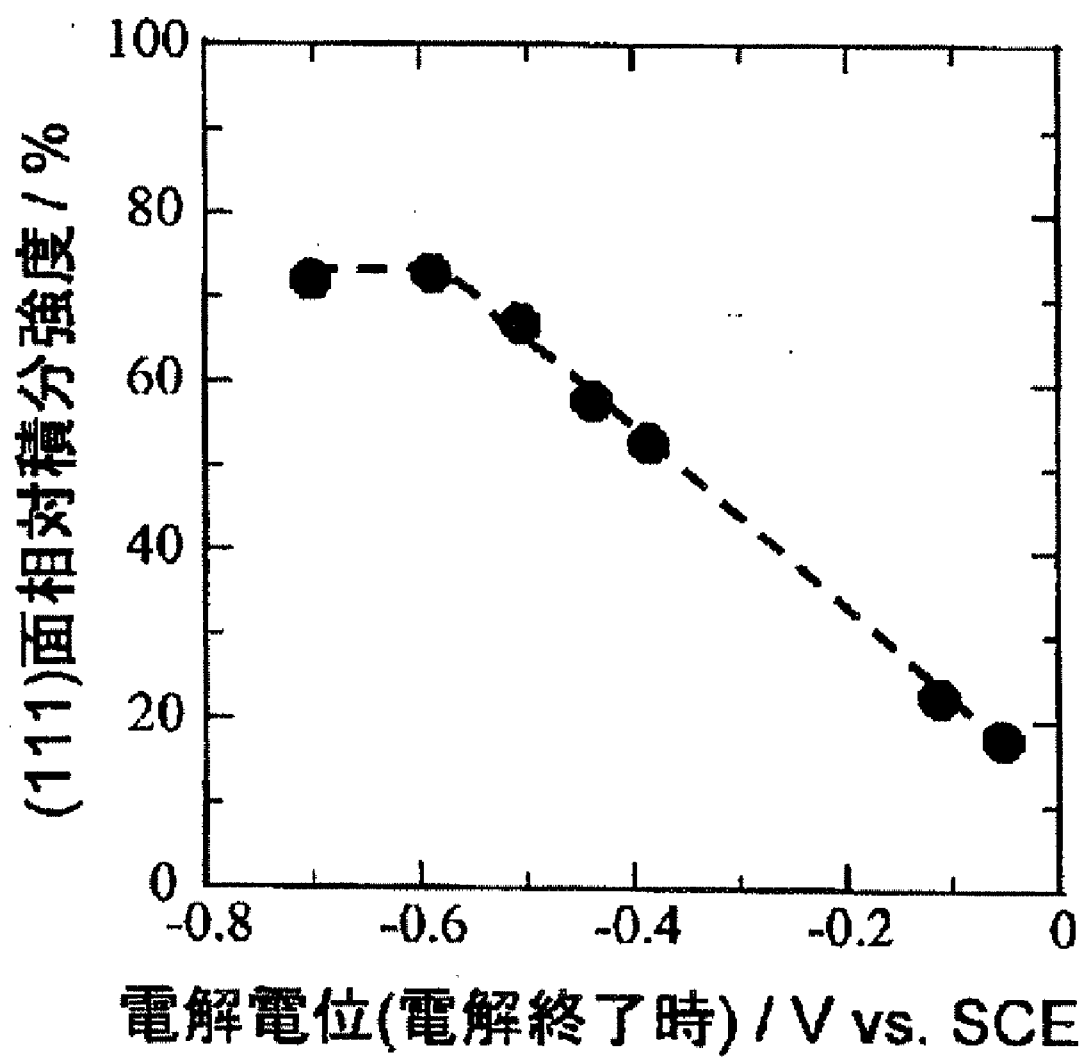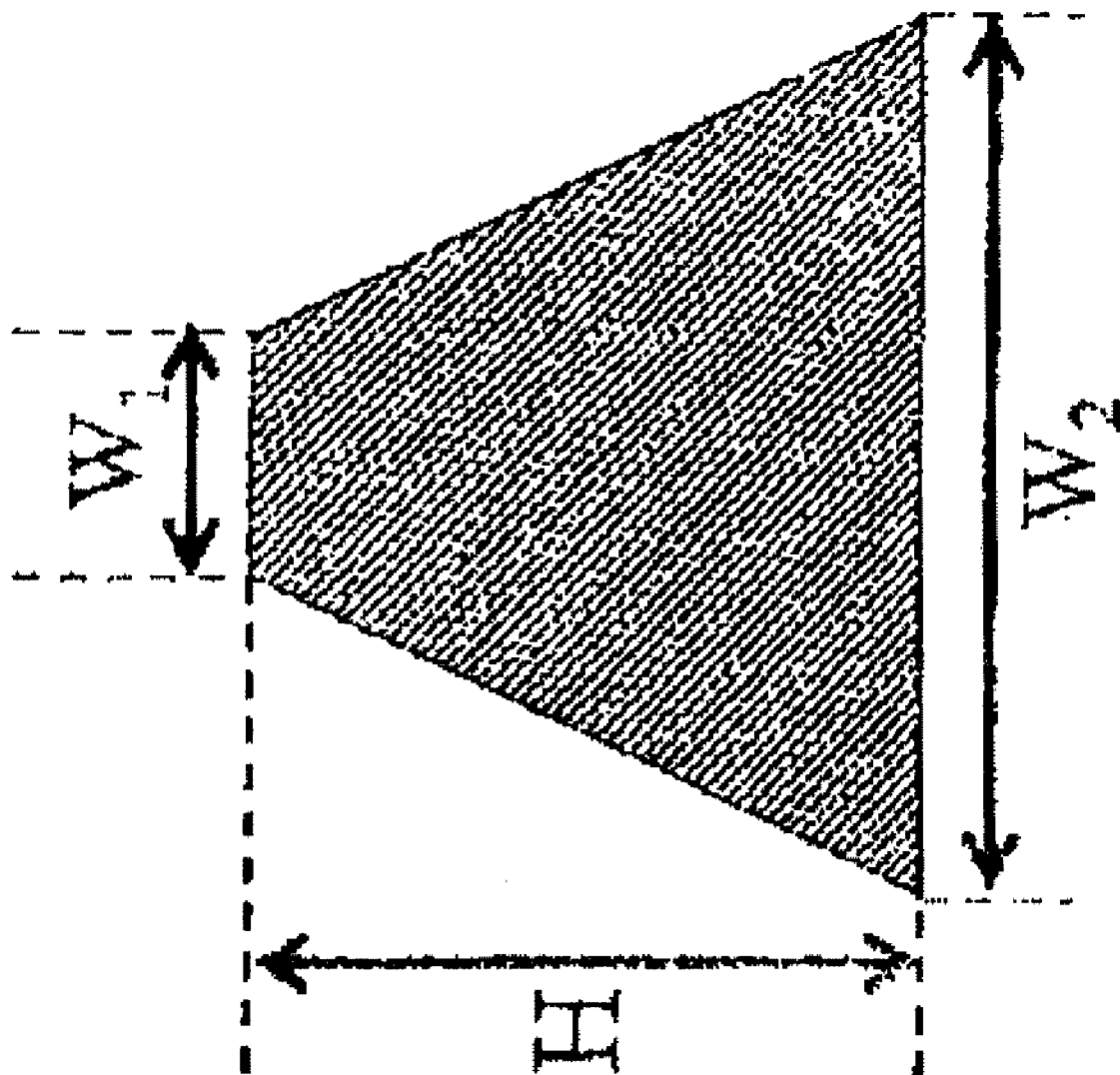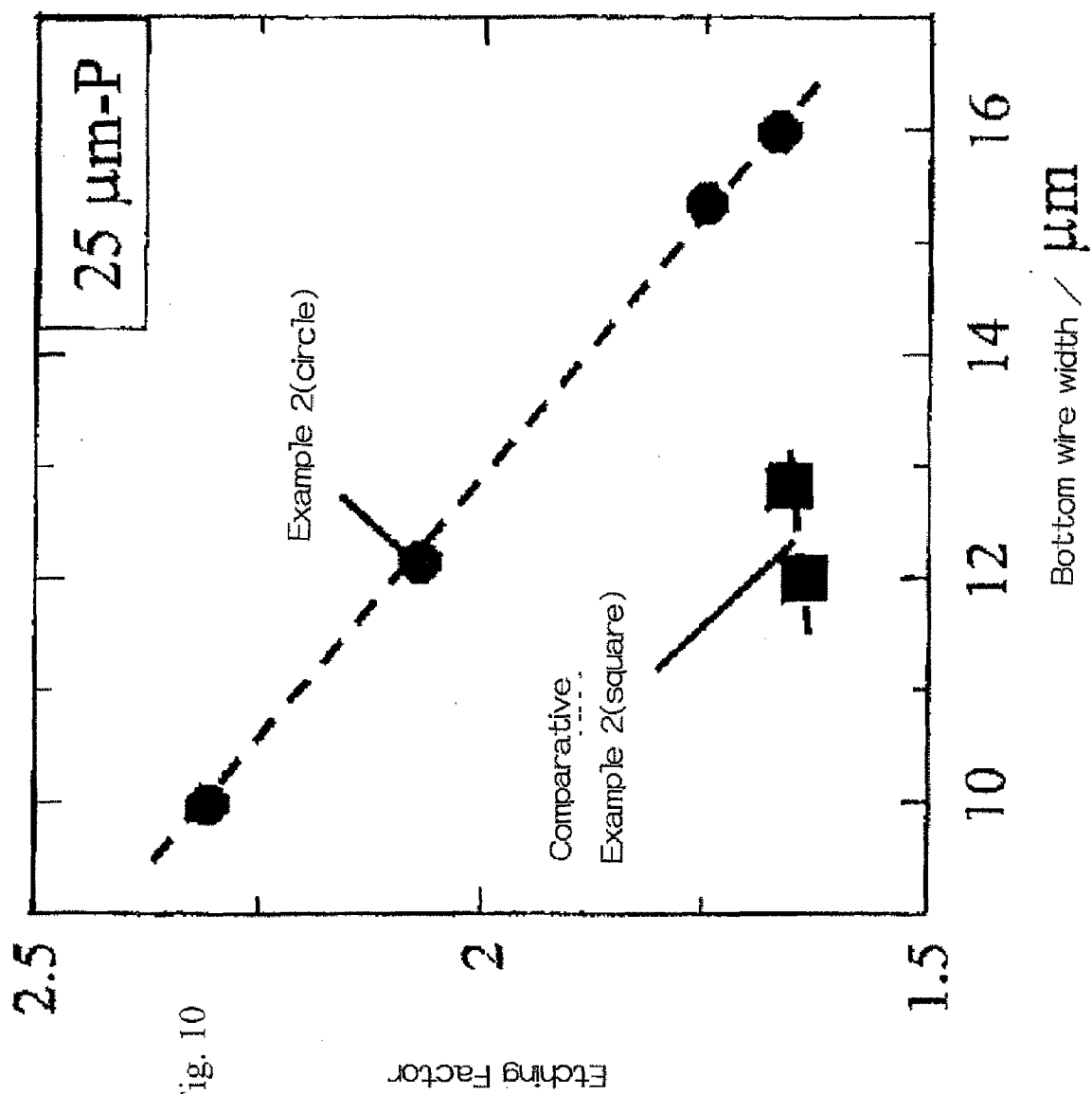ate plating method and chemical mechanical polishing technique) as the momentum, recently, development of a novel metal thin film fabrication method by electroplating is anticipated.

[0003] Copper is a crystal having a face centered cubic lattice (fcc) structure, the (111) plane is the densest face in which the copper atom arrangement becomes closely packed, thus by increasing the proportion of the (111) plane crystal orientation, pinholes occurring on the copper film surface can be suppressed, in addition, processability can be increased, such that, for instance, in the damascene method or the like, the possibility of manufacturing LSI wiring having satisfactory implantability into wiring gutter and excellent electromigration resistance is anticipated. In addition, there are also reports that etching properties become satisfactory by increasing the proportion of the (111) plane crystal orientation.

[0004] In prior art, based on the observation that the crystal orientation of a copper thin film is strongly influenced by the state of the substrate surface, a method has been proposed, whereby the surface of the substrate is irradiated with inert gas ions to treat the surface, then, a copper thin film is formed by the PVD method (physical vapor deposition method), as a method for increasing the proportion of the (111) plane crystal orientation (Patent Reference 1).

[0005] In addition, a method for forming a highly oriented (111) Cu film by a method using a URT-ion plating apparatus whereby a source metal is irradiated with a high-energy plasma, which has been highly densified by a high magnetic field, and vapor deposition particles obtained in this way are ionized and highly-energized by further passing through high-energy plasma to deposit a film on the substrate, and the like, have been also disclosed (Non-patent Reference 1).

[0006] In addition, a copper film preparation method in which the proportion of (111) plane orientation is increased by controlling to 2 10^{-6} Torr or less the degree of vacuum reached in a copper film preparation method by sputtering or vapor deposition inside a vacuum apparatus, and the like, have been also disclosed (Patent Reference 2)

[0007] As a method for increasing the (111) plane orientation by the electroplating method, for instance, a method is disclosed in Patent Reference 3, in which electroplating is carried out using an aqueous solution of copper fluorosilicate as the electrolytic solution to plate-deposit a strongly (111)-oriented copper thin film.

[0008] Patent Reference 1 Japanese Patent Application Laid-open No. H5-230626
[0009] Patent Reference 2 Japanese Patent Application Laid-open No. 16-275617
[0010] Patent Reference 3 Patent No. 3488193 (Japanese Patent Application Laid-open No. 2002-105687)
[0011] Non-Patent Reference 1 Tokuji Himuro at al. "Thermal Stability and Internal Stress in Highly Oriented Cu Film" Nippon Kinzoku Gakckaishi, Vol. 67, No. 7 (2003) 342-347.

DISCLOSURE OF THE INVENTION

[0012] The present invention relates to a method for producing a metal thin body by the electroplating method, and attempts to provide a novel method that may increase the (111) plane orientation of a metal thin body. In particular, since the relative integrated intensity of the (111) plane in non-oriented copper powder is approximately 55% (refer to ASTNP, to provide a metal thin body having a proportion of (111) plane orientation that is sufficiently high in comparison to this, a method for producing a copper thin body whereby the relative integrated intensity of the (111) plane may reach 65% or greater is attempted to be provided.

[0013] For such problem-solving, the present invention proposes an electrolytic solution (also referred to as "plating solution") containing water and a water-soluble organic solvent, concretely acetonitrile, and preferably an electrolytic solution containing 5% in volume or greater of acetonitrile and water, while at the same time, it proposes a method for producing a metal thin body by electroplating using this electrolytic solution.

[0014] Preparation of a Metal Thin Body by Such Electroplating Method Allows the orientation of the (111) plane in the metal thin body to be increased, and allows the relative integrated intensity of the (111) plane to be increased to 65% or greater. Here, "metal thin body" includes a metal film, a metal foil, or a tape, a sheet, or a metal plate, and the like, with no particular limitation on the thickness. For instance, included are metal thin bodies with a thickness of 0.1 μm to 50 mm, and also included are metal thin bodies in a layered state on a substrate.

[0015] In addition, for the above "metal of the metal thin body" (may also be referred to as plating metal in electroplating, or metal of metal ion in the electrolytic solution), besides various single metals, such as, zinc, cadmium, nickel, cobalt, chromium, tin, lead, solder, gold, silver, copper and rhodium, alloys thereof can be cited, and among of them, preferably, metals having a valence of two or greater or alloys thereof, for instance, metals belonging to the Group Ib, such as, copper, silver and gold, metals belonging to the Group VIII, such as, iron, cobalt and nickel, or alloys thereof may be cited, and among of them, metals having valences of +1 and +2 or alloys thereof, for instance copper and alloys thereof, can be cited as particularly desirable.

[0016] In addition, as the above "water-soluble organic solvent", that is to say, an organic solvent dissolving mutually with water, alcohols, such as, for instance, methanol, ethanol, n-propanol, isopropanol, isobutanol, ethylene glycol, dipropylene glycol and propylene glycol, ketones, such as, for

instance, acetone and ethylmethyl ketone, in addition, diethylene glycol, tetrahydrofuran, dioxane, or cyanogen series organic solvents, such as, acetonitrile, and the like, can be cited; among these, the present invention proposes acetonitrile as a particularly preferable "water-soluble organic solvent".

[0017]   In addition, the present invention proposes electroplating using an electrolytic solution containing 10% in volume or greater of acetonitrile and water, as a method for producing a metal thin body having 65% or greater of relative integrated intensity of the (111) plane.

[0018]   In so doing, the acetonitrile concentration in the electrolytic solution is preferably regulated to a range of 10 to 22% in volume. In addition, as the metal of the metal thin body, selecting a metal having a valence of two or greater or alloys thereof is preferred, and among of them, the metal with the lowest valence is preferably regulated to a concentration in the range of 0 to 0.08 mol/L in the electrolytic solution.

[0019]   Note that in the present invention "electroplating" includes all methods passing a current in an electrolytic solution containing an ionized metal to deposit a plating metal on the surface of a cathode.

[0020]   In addition, in the present invention, the statements "X to Y" (X and Y are any numbers) mean "X or greater but Y or less" unless otherwise mentioned, and simultaneously include the meaning "preferably greater than X and less than Y".

BRIEF DESCRIPTION OF THE DRAWINGS

[0021]   FIG. 1 X-ray diffractometry chart of a copper thin film obtained in the example.

[0022]   FIG. 2 X-ray diffractometry chart of a copper thin film obtained in the comparative example.

[0023]   FIG. 3 Graph showing the relationship between the quantity of acetonitrile (CH_3CN) added and the relative integrated intensity of the (111) plane.

[0024]   FIG. 4 Graph showing the relationship between the H_2SO_4 concentration and the relative integrated intensity of the (111) plane.

[0025]   FIG. 5 Graph showing the relationship between the concentration of Cu+ in the electrolytic solution and the relative integrated intensity of the (111) plane.

[0026]   FIG. 6 Graph showing the relationship between the current density and the relative integrated intensity of the (111) plane at each electrolytic solution temperature.

[0027]   FIG. 7 Graph showing the relationship between the current density and the relative integrated intensity of the (111) plane.

[0028]   FIG. 8 Graph showing the relationship between the electrolytic potential of the electrolysis and the relative integrated intensity of the (111) plane.

[0029]   FIG. 9 Explanatory figure to describe the measurement length used in the calculation of the etch factor.

[0030]   FIG. 10 Graph comparing etch factors in the samples obtained in Example 2 and Comparative Example 2.

EMBODIMENTS FOR CARRYING OUT THE INVENTION

[0031]   Hereinafter, a copper thin body preparation method will be described as one preferred example of embodiments of the present invention; however, the present invention is not to be limited by the embodiment described below.

[0032]   A method will be described as one preferred example of embodiments of the present invention, whereby electroplating is carried out using an electrolytic solution (also referred to as "plating solution") containing copper ion, acetonitrile and water to prepare a copper thin film (copper thin body).

[0033]   By carrying out electroplating to prepare a copper thin film using an electrolytic solution obtained by mixing acetonitrile, in particular an electrolytic solution obtained by mixing 5% or greater of acetonitrile, not only can a copper thin film having high proportion of (111) plane orientation be obtained, but also a smooth copper thin film with no hydrogen production over a broad current density region can be obtained. In addition, a copper thin film having a low enough specific resistance can also be formed.

[0034]   Note that, when carrying out electroplating to prepare a copper thin film using an electrolytic solution obtained by mixing acetonitrile, the current efficiency can be increased by adjusting the electrolysis conditions, allowing the copper thin film (copper thin body) to be prepared also in an electrically efficient manner. That is to say, by adding acetonitrile to the electrolytic solution, the state of the metal with the lower valence in which a metal has a valence of two or greater (in the case of copper, monovalent copper ion) can be stabilized in the electrolytic solution, allowing the rate of presence of the metal with the lowest valence to be raised. Consequently, as is apparent when comparing the following formulae (1) and (2), copper can be deposited with fewer amount of electricity, allowing the copper thin body to be prepared in an electrically efficient manner.

[0035]   With the proviso that, as shown below, since the concentration of the metal with the lower valence in which a metal has a valence of two or greater (in the case of copper, monovalent copper ion) in the electrolytic solution must be lowered in order to increase the proportion of the (111) plane orientation, raising the proportion of the (111) plane orientation and raising the current efficiency are in a trade-off relationship.

$$Cu^+ + e^- \rightarrow Cu \qquad (1)$$

$$Cu2^+ + 2e^- \rightarrow Cu \qquad (2)$$

[0036]   Electrolytic Solution

[0037]   The electrolytic solution used in the present embodiment (also referred to as "the present plating solution") must be an aqueous solution containing the copper ion to be electrodeposited and acetonitrile. For instance, aqueous solutions obtained by dissolving water-soluble cuprates, such as, alkaline copper cyanide and copper pyrophosphate and acidic copper borofluoride and copper sulfate, and acetonitrile, and the like, can be cited as preferred examples, and among of them, copper sulfate aqueous solution containing copper sulfate and sulfuric acid mixed with acetonitrile is preferred.

[0038]   As one concrete example, an electrolytic solution obtained by diluting with pure water an electrolytic solution containing a copper sulfate aqueous solution and acetonitrile to be adjusted to the desired composition concentration suited to the purpose is preferred.

[0039]   In addition, additives, such as, brightening agent, complexing agent, buffer agent, supporting electrolyte, organic compound (glue, gelatin, phenolsulfonic acid, white molasses and the like), multivalent alcohol and titanium, can be added to the electrolytic solution. In so doing, the quantity added is preferably a concentration of 1% in weight or less.

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[0040] Note that acetonitrile (CH_3CN) is a water-soluble organic cyanide compound referred to as ethane nitrile or methyl cyanide. Even when another water-soluble organic compound is used as the principal component instead of acetonitrile, the same effect as the effect of acetonitrile can be anticipated. In particular, regarding the point of increasing the ratio of monovalent copper ion present in the electrolytic solution, since the unshared electron pair on the acetonitrile can be presumed to have an effect, a water-soluble organic compound having an unshared electron pair can be anticipated to allow the current efficiency to be increased, similarly to acetonitrile.

[0041] Cathode

[0042] The material for the cathode used in the present embodiment, that is to say, the working electrode serving as the plated body, is not limited in particular. For instance, nickel, copper (sputter film), titanium, stainless steel plate and electrode plates made from other materials can be cited. Among of them, nickel, copper (sputter film), titanium plate, and the like, can be preferably indicated as examples.

[0043] Anode

[0044] The material as the anode used in the present embodiment, that is to say, the counter electrode, is not limited in particular. For instance, electrode plate made of copper can be preferably indicated as an example.

[0045] Electrolysis Conditions or the Like

[0046] The electrolysis conditions, or the like, in the present embodiment, will be explained. Here, in particular, explanations will be given centered on the electrolysis conditions to elevate to 65% or greater the relative integrated intensity of the (111) plane of the metal thin body (copper thin film) to be obtained.

[0047] Amount of Acetonitrile

[0048] It is sufficient that the concentration of acetonitrile in the electrolytic solution is in general 5% in volume or greater, and in particular 5 to 40% in volume. With the proviso that, to increase the relative integrated intensity of the (111) plane to 65% or greater, 10% in volume or greater, and in particular 10 to 20% in volume is necessary. In addition, the relative integrated intensity of the (111) plane can be brought to 70% or greater by bringing the concentration in the electrolytic solution to 10 to 15% in volume.

[0049] H_2SO_4 Concentration

[0050] As the H_2SO_4 concentration does not influence the relative integrated intensity of the (111) plane, it is not limited in particular.

[0051] Concentration of +1 Metal (Copper) in the Electrolytic Solution

[0052] It is sufficient that the concentration of +1 metal (copper) in the electrolytic solution, that is to say, the concentration of the metal with the lower valence in which a metal has a valence of two or greater in the electrolytic solution, is in general 0 to 0.15 mol/L, and to bring the relative integrated intensity of the (111) plane to 65% or greater, it is preferably regulated to 0 to 0.08 mol/L. Among of them, 0.07 mol/L or less is where the relative integrated intensity of the (111) plane can be brought to 70% or greater.

[0053] For the adjustment of the concentration of +1 metal (copper) in the electrolytic solution, adjustment is possible for instance by adjustment of the amount of the electrolytic solution (electrolytic solution not containing +1 metal (copper)) in circulation, adjustment of the electrolysis time, use of insoluble anode, and the like. With the proviso that, it is not limited to these methods.

[0054] Meanwhile, the concentration of +2 metal (copper) in the electrolytic solution, that is to say, the concentration of metals other than the metal with the lower valence in which a metal has a valence of two or greater in the electrolytic solution, although dependent on the current density, is preferably regulated in the range of 0.01 mol/L to 1 mol/L.

[0055] Electrolysis Temperature

[0056] The electrolysis temperature, that is to say, the temperature of the electrolytic solution, is not limited in particular. With the proviso that, from the point of view of decreasing the manufacturing costs and evaporation of organic constituent, a regulation to 25 to 45° C. is preferred.

[0057] Electrolytic Potential of the Electrolysis

[0058] It is sufficient that the electrolytic potential of the electrolysis is in general the electrolytic potential at which the metal deposits (more negative than equilibrium potential); however, to bring the relative integrated intensity of the (111) plane to 65% or greater, the electrolytic potential is preferably brought to more negative than –0.5V vs. SCE with no production of hydrogen.

[0059] Current Density

[0060] While the current density is not limited in particular, to bring the relative integrated intensity of the (111) plane to 65% or greater, it is preferably regulated to 0.005 A/cm^2 or greater. Although the upper limit value is not limited in particular, on the order of 1 A/cm^2 is thought to be a realistic upper limit value. More preferably, regulating the current density according to the electrolysis temperature is preferred; concretely, regulation to 0.005 to 0.02 A/cm^2 when the electrolysis temperature is 25° C. or greater and less than 35° C., and to 0.02 A/cm^2 or greater when the electrolysis temperature is 35° C. or higher, is preferred.

[0061] Electrolysis Time

[0062] The electrolysis time (electricity flowing time) is not limited in particular. The thickness of the copper thin body (copper thin film) can be regulated by adjusting the electrolysis time.

[0063] Film Forming Speed

[0064] The film forming speed is not limited in particular, and becomes 0.1 μm/min or greater when regulating with the ranges of the above conditions to bring the relative integrated intensity of the (111) plane to 65% or greater. For instance, when the current density is 0.005 to 1 A/cm^2, the film forming speed is 0.1 to 20 μm/min.

[0065] Summing the above points, as preferred conditions for producing a copper thin body with a relative integrated intensity for the (111) plane of the copper crystal of 65% or greater, electroplating with a concentration of acetonitrile in the electrolytic solution of 10 to 20% in volume, and, a concentration in the electrolytic solution of +1 copper of 0 to 0.08 mol/L, and, an electrolytic potential of the electrolysis of more negative than –0.5V vs. SCE, and, a current density regulated to 0.005 A/cm^2 or greater, can be given.

[0066] Copper Thin Film (Copper Thin Body)

[0067] According to the electroplating of the present embodiment, a copper thin film can be formed, having a strong (111) plane priority orientation, and a smooth surface, and sufficiently low specific resistance. In particular, as mentioned above, a copper film (layer) can be obtained, having a crystal orientation with a relative integrated intensity of the (111) plane of 65% or greater, preferably 70% or greater, and among of them, preferably 80% or greater. In so doing, since the thickness of the product can be adjusted by adjusting the electrolysis time (electricity flowing time), for instance, a 0.1

μm to 50 mm-thick copper thin body having a relative integrated intensity of the (111) plane of 65% or greater can be obtained.

[0068] Note that the relative integrated intensity of the (111) plane indicates the proportion (%) of the peak area of the (111) plane with respect to the sum of the peak areas of the (111) plane, the (200) plane, the (220) plane and the (311) plane in the X-ray diffractometry chart. In addition, according to the electroplating of the present embodiment, the relative integrated intensity of the (220) plane can be brought to 5 to 24%, the relative integrated intensity of the (220) plane to 3 to 12%, and the relative integrated intensity of the (311) plane to 4 to 15%.

[0069] Further in addition, the copper thin film obtained in the present embodiment is characterized by high purity. No acetonitrile remaining in the obtained copper thin film (product) even when acetonitrile is mixed in the electrolytic solution, is another characteristic of the present invention, therefore, a copper thin film with low concentration in impurity and sufficiently low specific resistance can be obtained.

[0070] The copper thin film (product) obtained in the present embodiment has characteristic such as described above, in particular, allows the orientation of the (111) plane to be increased, such that, for instance, the surface of the copper thin film (product) can be made smooth, and occurrence of pinholes can be suppressed, and furthermore, processability can be increased. Therefore, for instance, the possibility of manufacturing LSI wiring with satisfactory implantability into wiring gutter and excellent electro-migration resistance, in a damascene method, or the like, is anticipated. In addition, etching property can also be made satisfactory.

[0071] Thus, the copper thin film (copper thin body) obtained according to the present invention can be used as a metal film, a metal foil, a metal tape, a metal sheet, a metal plate, and the like, used in various applications, and, in particular, can be used in electronic material, for instance, mounting board for an IC or the like, electrode material for a film capacitor or the like, TAB tape, COF tape and the like.

[0072] As one concrete example, a circuit provided with a wiring (for instance, IC lead frame, print wiring plate, and the like) with a large etch factor (=etching distance in the depth direction/etching distance in the lateral direction) and small specific resistance can be formed due to the excellent etching property. For instance, by forming a copper thin layer (seed layer) by sputtering or the like over a substrate provided with electrical insulation properties, forming a copper thin film having a relative integrated intensity of the (111) plane of 65% or greater, preferably 70% or greater, and particularly preferably 80% or greater by electroplating method as described above to fabricate a substrate for circuit forming, forming an etching resist layer over the copper thin film of this substrate for circuit forming, and then, after exposure and development using a photo-mask for circuit pattern, dissolving and eliminating the exposed copper thin film using an etching solution that dissolves copper only to form a circuit pattern, allows a circuit provided with a copper wiring having a relative integrated intensity of the (111) plane of 65% or greater, preferably 70% or greater, and particularly preferably 80% or greater, to be formed.

[0073] In so doing, as the copper thin film of the above substrate for circuit forming allows the relative integrated intensity of the (111) plane to be 65% or greater, preferably 70% or greater, and particularly preferably 80% or greater,

with the excellent etching property, as verified in the following examples, wiring with a large etch factor can be formed, allowing a high density, high precision micro-circuit to be manufactured stably.

[0074] Note that, when manufacturing a copper thin film by electroplating using an electrolytic solution (present plating solution) obtained by mixing acetonitrile as in the present invention, the property of the plating to grow readily in the direction of the line of electric force (="eplating growth anisotropy") can be increased by adjusting the concentration of +1 metal (copper) in the electrolytic solution and the concentration of +2 metal (copper) in the electrolytic solution. Consequently, a wiring circuit in which the sides of the wiring are more perpendicularly shaped (=corresponding to a state where the etching factor in the etching is large) can be formed by the additive process, and the possibility of manufacturing a high density, high precision micro-circuit is expected. For instance, a copper thin layer (seed layer) is formed by sputtering or the like over a substrate provided with electrical insulation properties, thereabove, a plating resist with the desired pattern is formed, the pattern of the seed layer is formed by etching, and plating copper is grown in a direction perpendicular to the seed layer pattern. In so doing, carrying out copper plating using an electrolytic solution obtained by mixing acetonitrile as described above and adjusting the electrolytic solution concentrations of +1 and +2 metals (copper), and then, dissolving the resist to form the circuit pattern, allows the possibility of manufacturing a micro-circuit in which the sides of the wiring are more perpendicularly shaped.

[0075] In addition, it is also possible to form a circuit pattern seed with an inkjet printer using a metallic ink, and then, grow the copper circuit similarly to the previous method with the present plating solution. Even without using a metallic ink, it is also possible to draw with an inkjet printer a catalyst for non-electrolytic plating, for instance, a Sn solution or a Pd solution, in the pattern of the circuit to be formed, form a thin Cu film by non-electrolytic plating, and then, with this as the seed, form a thick film circuit by plating similarly to above. In addition, not only the inkjet printer method, but also various printing methods in which a circuit is designed (screen printing, gravure printing, and the like), may be used in the circuit pattern formation for the seed formation thereof. In addition, it may be a method such as imprinting technique.

[0076] "Plating growth anisotropy" can be adjusted, as mentioned above, can also be phrased as plating homogeneity (throwing power) can be adjusted by controlling the concentration of +1 metal (copper) in the electrolytic solution and the concentration of +2 metal (copper) in the electrolytic solution, viewed from the opposite point of view. Consequently, while electroplating is generally difficult in narrow places such as microscopic grooves or holes as the activity of ions becomes less, the homogeneity of plating can be increased by controlling the concentrations of +1 and +2 metals (copper) in the electrolytic solution, allowing homogeneous plating also in such locations to be anticipated.

[0077] The technical thinking of the present invention, that is to say, the technical thinking of electroplating using an electrolytic solution obtained by mixing acetonitrile, can also be anticipated to be applied to non-electrolytic plating. For instance, there is a possibility of forming a metal thin body with a high proportion of (111) plane orientation by carrying out non-electrolytic plating with acetonitrile mixed in a plating solution containing a reducing agent, allowing effects not

obtained in generic non-electrolytic plating to be anticipated. In general, to form a copper layer over a substrate provided with electrical insulation properties, physical methods such as sputtering or methods by non-electrolytic plating are adopted; however, non-electrolytic plating, which does not used vacuum process, is more advantageous cost-wise.

[0078] It is by mixing acetonitrile to this non-electrolytic plating solution that a special plating film with a larger proportion of the (111) plane crystal orientation is obtained. In particular, in the so-called damascene process, while normally an insulation film is formed over a substrate comprising a silicon wafer or the like, grooves and holes are formed in the insulation film where wiring pattern formation is planned, and a copper thin layer (seed layer) to obtain conduction is formed by a physical method such as PVD, it can be anticipated that according to non-electrolytic plating with a plating solution with acetonitrile mixed, copper is directly implanted in these grooves and holes, allowing copper wiring to be formed. As throwing power of non-electrolytic plating with acetonitrile mixed is satisfactory, it is convenient for micro-circuit implantation. In addition, from a similar line of thought, this electrolytic solution with acetonitrile mixed can be also used as a non-electrolytic plating bath for through-hole plating of a circuit substrate.

EXAMPLE

Example 1

[0079] An electrolytic solution obtained by mixing a copper sulfate aqueous solution and acetonitrile was diluted with pure water to prepare an electrolytic solution having a Cu^{2+} concentration of 0.1 mol/L, an H_2SO_4 concentration of 0.6 mol/L and a CH_3CN concentration of 32% in volume, and electroplating was carried out under the following conditions:

[0080] Cathode: nickel plate

[0081] Anode: pure copper plate

[0082] Electrolysis temperature (solution temperature): 25° C.

[0083] Current density: 0.005 A/cm^2

[0084] Electrolysis time (electricity flowing time): 1.5 hours

[0085] Note that from the evaluation results during electro-plating and after electroplating, the electrolytic potential of the electrolysis was −0.640V vs. SCE, the film thickness of the copper film was approximately 14 μm, the film forming speed was approximately 0.15 μm/min, and the concentration of Cu^+ in the electrolytic solution was 0.07 mol/L.

Comparative Example 1

[0086] Electroplating was carried out similarly to the above example, except that acetonitrile was not added.

[0087] XRD analysis was carried out under the following conditions (FIG. 1 and FIG. 2) on the copper thin films obtained in the above examples and the above comparative examples to determine the relative integrated intensities of the (111) plane as well as the (220) plane.

[0088] For instance, for the relative integrated intensity of the (111) plane, the peak areas of the (111) plane, the (200) plane, the (220) plane and the (311) plane were determined in the (111) chart, and it was calculated as the proportion (%) of the peak area of the (111) plane relative to the sum of these peak areas. The calculation method for the (220) plane was identical.

[0089] <XRD Measurement>

[0090] The copper thin films obtained in the examples and comparative examples served as samples for X-ray diffracto-metry.

[0091] Samples for X-ray diffractometry were attached to a holder and measured using RU-200 (manufactured by RIGAKU Corporation) under the following conditions:

[0092] (X-ray tube) CuK alpha

[0093] (tube voltage) 40 kV

[0094] (tube current) 150 mA

[0095] (sampling interval) 0.02°

[0096] (scan speed) 4.0°/min

[0097] (start angle) 30°

[0098] (end angle) 100°

[0099] Test 1: Acetonitrile Concentration

[0100] Under the conditions of the above example, the relative integrated intensity of the (111) plane when the amount of acetonitrile added was varied in the range of 0 to 40% in volume was determined and shown in FIG. 3.

[0101] As a result, it was found that when electroplating using an electrolytic solution with acetonitrile mixed, the orientation of the (111) plane became strong, that when the amount of acetonitrile added reached 10% in volume, the relative integrated intensity of the (111) plane increased prominently, and that by bringing it to 10 to 20% in volume, the relative integrated intensity of the (111) plane could be brought to 65% or greater.

[0102] In addition, it was also found that by bringing it to 10 to 15% in volume, the relative integrated intensity of the (111) plane could be brought to 70% or greater.

[0103] Test 2: H_2SO_4 Concentration

[0104] Under the conditions of the above example, the relative integrated intensity of the (111) plane when the H_2SO_4 concentration was varied in a range of 0.2 to 0.6 mol/L was determined and shown in FIG. 4.

[0105] As a result, it was found that the H_2SO_4 concentration did not influence the orientation of the (111) plane.

[0106] Test 3: Cu^+ Concentration

[0107] Under the conditions of the above example, the relative integrated intensity of the (111) plane when the Cu^+ concentration was varied by adjusting the electrolysis time was determined and shown in FIG. 5.

[0108] As a result, it was found that the higher the Cu^+ concentration, the weaker the orientation of the (111) plane became, and that a regulation to 0 to 0.05 mol/L was preferable to bring the relative integrated intensity of the (111) plane to 65% or greater.

[0109] Test 4: Electrolytic Solution Temperature

[0110] Under the conditions of the above example, the relationship between the current density and the relative integrated intensity of the (111) plane when electrolysis was carried out at the electrolytic solution temperature of 25° C., 35° C. and 45° C. was determined and shown in FIG. 6.

[0111] As a result, it was found that the higher the electrolytic solution temperature, the weaker the orientation of the (111) plane became, when comparing at the same current density. With the proviso that, when the electrolytic solution temperature was high, it was found that the orientation of the (111) plane could be enhanced by increasing the current density (bringing the electrolytic potential of the electrolysis to more negative).

[0112] In addition, it was found that when the electrolysis temperature was 25° C. or higher but less than 35° C., regulation to 0.005 to 0.02 A/cm^2 was desirable and that when the electrolysis temperature was 35° C. or higher, a regulation to

0.02 A/cm^2 or greater was desirable in order to bring the relative integrated intensity of the (111) plane to 65% or greater.

[0113] Test 5: Current Density

[0114] Under the conditions of the above example, the relative integrated intensity of the (111) plane when the current density was varied in a range of 0.005 to 0.05 A/cm^2 was determined and shown in FIG. 7.

[0115] As a result, a tendency was observed for the orientation of the (111) plane to become stronger when the current density was higher, and it was found that a regulation so as to bring it to 0.005 to 0.02 A/cm^2 was desirable to bring the relative integrated intensity of the (111) plane to 65% or greater.

[0116] Test 6: The Electrolytic Potential of the Electrolysis

[0117] Under the conditions of the above example, the relative integrated intensity of the (111) plane when the electrolytic potential of the electrolysis was varied in a range of 0 to −0.7V vs. SCE was determined and shown in FIG. 8.

[0118] As a result, a tendency was observed for the orientation of the (111) plane to become stronger when the electrolytic potential of the electrolysis is more negative, and it was found that regulating the electrolytic potential of the electrolysis to be more negative than −0.5V vs. SCE was desirable to bring the relative integrated intensity of the (111) plane to 65% or greater.

Example 2

[0119] A tape-shaped sample was prepared, obtained by forming a nickel-chromium layer over polyimide, and 0.2 μm of copper formed thereabove as a seed layer (polyimide substrate with a copper seed), and a copper thin film layer (8 μm) was formed by electroplating to this tape-shaped sample using the following electrolytic solution under the following conditions to fabricate a substrate for circuit forming.

[0120] An electrolytic solution obtained by mixing a copper sulfate aqueous solution and acetonitrile was diluted with pure water to prepare an electrolytic solution having a Cu^{2+} concentration of 0.1 mol/L, an H$_2$SO$_4$ concentration of 0.4 mol/L and a CH$_3$CN concentration of 10%, and electroplating was carried out under the following conditions:

[0121] Cathode: polyimide substrate with a copper seed

[0122] Anode: pure copper plate

[0123] Electrolysis temperature (solution temperature): 25° C.

[0124] Current density: 0.005 A/cm^2

[0125] Electrolysis time: 1.2 hours

[0126] Next, using a spin coater, liquid resist was applied onto the sample surface so as to obtain a thickness of approximately 1 μm over the copper thin film layer of the substrate for circuit forming, and after drying for one hour at 100° C., direct exposure was carried out via the glass mask printed into a circuit pattern (pitch: 25 μm).

[0127] The sample after exposure was developed and dried for two hours at 120° C. The exposed copper thin film layer of the sample after drying, was dissolved and eliminated by using a copper chloride etching solution (Cu: 134 g/L, HCl: 90 g/L) at 35° C., by varying the etching time to 25 seconds, 30 seconds, 35 seconds and 40 seconds. Thereafter, the resist was eliminated using acetone and CuCl residues were

removed by immersion for 10 seconds in a soft etching solution at 40° C. to form a circuit pattern, and 4 types of samples were obtained.

Comparative Example 2

[0128] Using a commercially-available substrate for circuit forming (product from company S) comprising an Ni series metal layer, a Cu seed layer and a copper thin film layer (approximately 8 μm) sequentially formed over a substrate made of polyimide, an etching resist layer was formed similarly to described above, then, etching was performed similarly to described above to form a circuit pattern, and a sample was obtained.

[0129] <Comparison of Etch Factors>

[0130] The obtained circuit patterns (samples) were observed by SEM, W$_1$ and W$_2$ shown in FIG. 9 were measured, and etch factors were determined according to the following Formula (1) and shown in FIG. 10.

$$\text{Etch factor (E.F.)} = H/[(W_2 - W_1)/2] \qquad (1)$$

[0131] From FIG. 10, it was revealed that, compared to the product from company S already commercialized substrate for circuit forming, the substrate for circuit forming obtained in Example 2 had a prominently large etch factor, and had excellent etching properties.

1. A method for producing a metal thin body, wherein electroplating is carried out using an electrolytic solution containing 5% in volume or greater of acetonitrile and water.

2. A method for producing a metal thin body having a relative integrated intensity of the (111) plane of 65% or greater, wherein electroplating is carried out using an electrolytic solution containing 10% in volume or greater of acetonitrile and water.

3. The metal thin body producing method as recited in claim 2, wherein the concentration of acetonitrile in the electrolytic solution is regulated to a range of 10 to 22% in volume.

4. The metal thin body producing method as recited in claim 1, wherein the metal of the metal thin body is a metal having a valence of two or greater, or alloys thereof, and among of them, the metal with the lowest valence is regulated to a concentration in the electrolytic solution in the range of 0 to 0.08 mol/L.

5. The metal thin body producing method as recited in claim 1, wherein the metal of the metal thin body is a metal belonging to group Ib or group VIII, or alloys thereof.

6. The metal thin body producing method as recited in claim 1, wherein electroplating is carried out using an electrolytic solution containing an additive in addition to acetonitrile and water.

7. A metal thin body having a relative integrated intensity of the (111) plane 65% or greater obtained by the producing method as recited in claim 4.

8. A plating solution containing acetonitrile and water.

9. A method for producing a copper thin body having a relative integrated intensity of the (111) plane of 65% or greater, wherein electroplating is carried out using an electrolytic solution containing water and acetonitrile and copper

sulfate, while at the same time, the concentration of acetonitrile in the electrolytic solution is regulated to 10 to 20% in volume, and, concentration of +1 copper ion in the electrolytic solution is regulated to 0 to 0.08 mol/L, and, the electrolytic potential of the electrolysis is regulated to more negative than –0.5V vs. SCE, and, the current density is regulated to 0.005 A/cm^2 or greater.

10. A copper thin body having a relative integrated intensity of the (111) plane of 65% or greater obtained by the producing method as recited in claim **9**.

11. A circuit provided with a copper wiring having a relative integrated intensity of the (111) plane of 65% or greater.

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