DESCRIPTION

Title of the Invention: INSOLUBLE-ANODE PLATING EQUIPMENT

FIELD OF THE INVENTION

[0001]

The present invention relates to an insoluble-anode plating equipment.

DESCRIPTION OF THE RELATED ART

[0002]

Conventionally, various plating processes have been performed on objects to be plated such as a semiconductor wafer and a printed wiring board. A so-called jet plating equipment is known to be used in the case of performing a plating process on such an object to be plated.

[0003]

Generally, this jet plating equipment includes: an opening part in which an object to be plated can be placed; a solution supply piping that supplies a plating solution toward the object to be plated; and an anode that is disposed to face the object to be plated. This jet plating equipment performs a plating process while supplying the plating solution from the solution supply piping toward the object to be plated. The jet plating equipment can perform a uniform plating process on a surface to be plated of the object to be plated, and can perform the plating process while sequentially replacing objects to be plated disposed in the opening part. Hence, the jet plating equipment is widely utilized as equipment suitable for small-lot production and plating process automation.

[0004]

Although this jet plating equipment has such advantages as described above, in the case where a soluble anode is used, a coating film formed on the anode surface, for example, a black film or the like, comes off to become an impurity in the plating solution, the impurity flows together with the plating solution supplied toward the object to be plated, and this exerts a harmful effect on the plating process in some cases.

[0005]

Moreover, air mixed in the solution and air bubbles generated from the anode reach the surface to be plated, and hinder a favorable plating process in other cases. Therefore, for this jet plating equipment, a method of arranging, in a plating tank, a separating membrane for separating the object to be plated and the anode from each other is known (see Patent Document 1 and Patent Document 2).

[0006]

If an insoluble anode is used, the jet plating equipment including the separating membrane has various merits compared with the case where the soluble anode is used. For example, the consumption amounts of additives in the plating solution can decrease. Moreover, maintenance such as anode replacement, which is required in the case where the soluble anode is used, is not required, and hence the productivity can be improved.

[0007]

However, although the jet plating equipment in which the insoluble anode is used has various merits as described above compared with the case where the soluble anode is used, under present circumstances in the plating field, the utilization of this jet plating equipment has made little progress, except for precious metal plating and copper plating.

[0008]

If the separating membrane is disposed in the plating tank in the jet plating equipment, an upper catholyte chamber is formed on the upper side of the separating membrane by the object to be plated placed in the opening part and the separating membrane, and a lower anolyte chamber is formed on the lower side of the separating membrane by the plating tank and the separating membrane. Then, because the insoluble anode is disposed in the lower anolyte chamber, many air bubbles are generated on the lower side of the separating membrane by gas generation due to electrolysis of water at the time of the plating process. Therefore, it is necessary to efficiently discharge the air bubbles generated on the lower side of the separating membrane. Moreover, although there may be cases where different types of solutions are separately supplied to the upper catholyte chamber and the lower anolyte chamber, in order to obtain the merits in the case where the insoluble anode is used, it is necessary to prevent the different types of solutions supplied to the upper catholyte chamber and the lower anolyte chamber from mixing with each other, with the separating membrane disposed in the plating tank.

[0009]

In Patent Document 1 of the related art, because a pressure loss at the time of the solution supply to the upper catholyte chamber is large, the supply flow rate to the lower anolyte chamber cannot be made appropriately large, and there is a tendency that the many air bubbles generated from the insoluble anode cannot be sufficiently discharged. Moreover, in Patent Document 2, although the air bubbles can be efficiently discharged in the lower anolyte chamber, the solution supplied to the upper catholyte chamber and the lower anolyte chamber cannot be separated, and hence the merits of the insoluble anode cannot be sufficiently realized.

[0010]

To solve such problems of the insoluble anode jet plating equipment in which the separating membrane is disposed in the plating tank, the related art described in Patent Document 3 (WO2022/107551) is proposed. In the technique described in Patent Document 3, there is no possibility of solutions supplied into the upper catholyte chamber and the lower anolyte chamber mixing, and air bubbles generated from the insoluble anode in the lower anolyte chamber can be efficiently discharged, and hence the merits of the insoluble anode can be sufficiently realized.

[0011]

When a copper plating process, for example, is performed with the plating equipment that uses the insoluble anode, it is necessary to adjust the copper concentration in the plating solution, as the copper is consumed in the plating process. As one method for adjusting the copper concentration, a method that uses copper oxide powder is proposed (Patent Document 4). The related art of Patent Document 4 proposes a technique in which copper oxide powder with a specified content of impurities, such as sodium, is used, and the copper concentration in the plating solution is controlled within a predetermined range by periodically adding copper oxide powder to the plating solution, so that a favorable copper plating process can be performed on a semiconductor substrate, such as a wafer.

Prior Art Document

Patent Document

[0012]

Patent Document 1

Japanese Patent Application Laid-Open No. 2000-273693

Patent Document 2

Japanese Patent Application Laid-Open No. 2007-169773

Patent Document 3

International Publication No. WO2022/107551

Patent Document 4

Japanese Patent Application Laid-Open No. 2018-62453

SUMMARY OF THE INVENTION

[Technical Problem]

[0013]

As described above, the plating equipment in which the insoluble anode is used has various merits compared with the case where the soluble anode is used, and hence various plating process techniques that can sufficiently employ such merits have been proposed. However, there has been a demand for further technical development for this plating equipment that uses an insoluble anode.

[0014]

Although a hole filling copper plating process for fine vias has been performed on objects to be plated, such as semiconductor wafers, in recent years, there has been further progress in reduction in weight, thickness, and length of electronic substrates or the like. For example, the size of vias has been remarkably reduced. Accordingly, there has been a demand for plating equipment that can uniformly perform a favorable copper plating process on, for example, fine vias with a high aspect ratio, such as a via diameter of 5 μm and a via depth of 100 μm. In the case where such a precision copper plating process is performed with the insoluble-anode plating equipment, it is extremely important to control concentrations of copper and additives in the plating solution. To be more specific, in the case where a copper sulfate solution is used as the plating solution in performing the copper plating process on a semiconductor wafer, additives (commercial products) called an

accelerator (promotor), a suppressor (inhibitor), and a leveler (smoother) are added to the plating solution. Such additives are liable to be consumed as the plating process continues, and additives are also consumed in the same manner in the insoluble-anode plating equipment in which the separating membrane is disposed. In the insoluble-anode plating equipment in which the separating membrane is disposed, a copper sulfate solution is supplied as the cathode plating solution to the upper catholyte chamber, which is formed by the separating membrane, and the copper concentration in the cathode plating solution decreases as the copper plating process continues. When the copper concentration in the copper sulfate solution decreases, sulfate ions (SO_4^{2-}) relatively increase. In the copper sulfate solution in which the sulfate ions relatively increase, additives in the solution is liable to be significantly consumed and, as a result, it becomes difficult to uniformly perform a favorable copper plating process. Particularly in the case where the copper plating process is performed on fine vias, fine trenches, or the like with a high aspect ratio, since a copper plating thickness is extremely small, in order to uniformly and continuously perform the copper plating process with a small thickness, it is necessary to suppress a fluctuation in copper concentration in the plating solution or to suppress the consumption of additives as much as possible. That is, there has been a demand for an insoluble-anode plating equipment that can continuously perform the copper plating process with a fluctuation in copper concentration in the copper sulfate solution as the plating solution being suppressed as much as possible.

[0015]

The present invention has been made under the above-mentioned circumstances, and it is an object of the present invention to provide an insoluble-anode plating equipment that can uniformly and continuously

perform a favorable copper plating process on fine vias, fine trenches, or the like with a high aspect ratio by suppressing a fluctuation in copper concentration in the cathode plating solution as much as possible, and by suppressing the consumption of additives contained in the cathode plating solution in performing the copper plating process on an object to be plated, such as a semiconductor wafer, with the insoluble-anode plating equipment in which the separating membrane is disposed.

[Solution to Problem]

[0016]

In order to solve the above-mentioned problem, the present invention relates to an insoluble-anode plating equipment provided with a plating tank including: an opening part in which an object to be plated is placed; a solution supply piping that supplies a plating solution toward the object to be plated; an insoluble anode that is disposed to face the object to be plated; and a separating membrane for separating the object to be plated and the insoluble anode from each other, a separating membrane outer peripheral end being fixed to a plating tank inner wall, a through-hole being provided in a separating membrane center, a hole peripheral end of the through-hole being fixed to the solution supply piping, the separating membrane being thus disposed so as to be inclined upward in a direction toward an outer periphery of the separating membrane from the solution supply piping, the solution supply piping supplying a cathode plating solution to an upper catholyte chamber in the plating tank from a control tank in which the cathode plating solution is stored, the upper catholyte chamber being formed by the separating membrane and the object to be plated that is placed, an anode solution being supplied to a lower anolyte chamber in the plating tank from an anode solution tank in which the anode solution is stored, the lower anolyte chamber being formed below the separating membrane, wherein the

insoluble-anode plating equipment includes a copper oxide powder supply unit configured to supply copper oxide powder to the control tank together with a carrier gas via a supply tube having an ability to remove static electricity, and an upper lid body of the control tank is provided with a powder supply cylinder having an ability to remove static electricity, and having a leading end disposed in a vicinity of a liquid surface of the cathode plating solution stored in the control tank, and the supply tube is connected to the powder supply cylinder.

[0017]

According to the present invention, an amount of copper oxide powder corresponding to the amount of copper used in the plating process is supplied to the cathode plating solution, and hence the copper concentration can be continuously maintained within a set copper concentration range. Accordingly, it is possible to reliably suppress the consumption of additives caused by a fluctuation in copper concentration during the plating process. As a result, a favorable copper plating process can be uniformly and continuously performed even on fine vias, fine trenches, or the like with a high aspect ratio. In the present invention, copper oxide powder is supplied to the cathode plating solution from the powder supply cylinder having an ability to remove static electricity and having the leading end disposed in the vicinity of the liquid surface of the cathode plating solution stored in the control tank. The reason for this is to cause a powdery copper oxide to be reliably charged into the cathode plating solution. When the leading end of the powder supply cylinder is distant from the liquid surface of the cathode plating solution stored in the control tank, of copper oxide powder supplied from the powder supply cylinder, a large amount of the copper oxide powder scatters into the space above the liquid surface of the cathode plating solution, thus making it difficult to adjust the copper concentration. In addition, when the leading end

of the powder supply cylinder contacts the liquid surface, copper oxide powder aggregates and adheres to the leading end portion, thus making it difficult to supply the copper oxide powder. For this reason, in the present invention, the leading end of the powder supply cylinder is disposed in the vicinity of the liquid surface of the cathode plating solution stored in the control tank. The term "vicinity" refers to a distance at which the leading end does not contact the liquid surface, but at which the copper oxide powder supplied from the leading end is prevented from scattering into the space above the liquid surface of the cathode plating solution. Although this distance between the leading end of the powder supply cylinder and the liquid surface of the cathode plating solution is suitably adjustable depending on the physical properties, such as average particle size, of copper oxide powder to be used, it is preferable that the distance be 50 to 100 mm.

[0018]

The present invention also relates to an insoluble-anode plating equipment provided with a plating tank including: an opening part in which an object to be plated is placed; a solution supply piping that supplies a plating solution toward the object to be plated; an insoluble anode that is disposed to face the object to be plated; and a separating membrane for separating the object to be plated and the insoluble anode from each other, a separating membrane outer peripheral end being fixed to a plating tank inner wall, a through-hole being provided in a separating membrane center, a hole peripheral end of the through-hole being fixed to the solution supply piping, the separating membrane being thus disposed so as to be inclined upward in a direction toward an outer periphery of the separating membrane from the solution supply piping, a cathode plating solution being supplied to an upper catholyte chamber in the plating tank via the solution supply piping from a control tank in which the cathode plating solution is stored, the upper

catholyte chamber being formed by the separating membrane and the object to be plated that is placed, an anode solution being supplied to a lower anolyte chamber in the plating tank from an anode solution tank in which the anode solution is stored, the lower anolyte chamber being formed below the separating membrane, wherein the insoluble-anode plating equipment includes a copper concentration adjustment tank configured to adjust a copper concentration in the cathode plating solution, the copper concentration adjustment tank includes a copper oxide powder supply equipment configured to convey copper oxide powder together with a carrier gas via a supply tube having an ability to remove static electricity, an upper lid body of the copper concentration adjustment tank is provided with a powder supply cylinder having an ability to remove static electricity, and having a leading end disposed in a vicinity of a liquid surface of the cathode plating solution stored in the copper concentration adjustment tank, and the copper concentration adjustment tank is provided with a stirring unit configured to stir the cathode plating solution, the supply tube is connected to the powder supply cylinder, and the copper concentration in the cathode plating solution in the copper concentration adjustment tank is adjusted by supplying the copper oxide powder to the copper concentration adjustment tank, and the cathode plating solution, the copper concentration of which is adjusted, is supplied to the control tank from the copper concentration adjustment tank.

[0019]

Although the insoluble-anode plating equipment of the present invention is preferably used for the copper plating process performed on an object to be plated, such as a semiconductor wafer, the object to be plated, such as a semiconductor wafer, is manufactured in a so-called cleanroom, and hence there may be cases where a substance that easily scatters, such

as copper oxide powder, causes contamination in the cleanroom. In view of the above, the copper concentration adjustment tank is disposed outside the cleanroom, and the copper concentration is adjusted in this copper concentration adjustment tank using copper oxide powder, and the adjusted cathode plating solution is supplied to the control tank. With such a configuration, contamination in the cleanroom can be reliably prevented.

[0020]

In the present invention, it is preferable that the copper oxide powder have an average particle size of 25 to 40 μm, and a packed bulk density of less than 1.7 g/cm^3. When a packed bulk density is equal to or more than 1.7 g/cm^3, dissolution of the copper oxide powder into the cathode plating solution is liable to slow down. It is more preferable that a packed bulk density be equal to or more than 1.5 g/cm^3 and less than 1.7 g/cm^3. Note that packed bulk density refers to the bulk density obtained as follows. Copper oxide powder is gently charged into a predetermined container, gaps within the powder are eliminated by applying a particular vibration to the container, and copper oxide powder is then charged again and, thereafter, the bulk density is measured. The packed bulk density in the present invention is a numerical value measured with a graduated cylinder. In addition, it is preferable that the copper oxide powder in the present invention have a relatively small angle of repose (10° to 12.5°). This angle of repose is obtained as follows. All of 100 mL of copper oxide powder, the packed bulk density of which is measured with a graduated cylinder, is dropped from a height of 15 cm to form a lump of copper oxide powder in a state of being piled in a mountain shape, and the angle of the skirt of the mountain-shaped lump is measured. When copper oxide powder has a large angle of repose, the copper oxide powder is liable to have a low dissolution rate. This angle of repose is indicative of fluidity of copper oxide powder and, when copper

oxide powder has an angle of repose of 10° to 12.5°, the copper oxide powder has high solubility. Gaps within the powder are formed due to geometrical factors of particle shape, or factors due to surface properties, such as adhesion. The present inventors have found that when a packed bulk density of copper oxide powder is approximately 1.6 g/cm^3, dissolution of the copper oxide powder in the cathode plating solution proceeds smoothly. The present inventors also found that when copper oxide powder has a granular particle shape, dissolution of the copper oxide powder proceeds smoothly. It is deemed that this relates to a fact that copper oxide powder has a relatively small angle of repose (10° to 12.5°).

[0021]

Although the powder supply cylinder of the present invention has an ability to remove static electricity, the powder supply cylinder that can be preferably used is one that is grounded (earthed), and made of titanium, or one to which a static eliminator (ionizer) is connected. When static electricity is generated on the powder supply cylinder, aggregation of copper oxide powder is liable to occur, so that it becomes difficult to supply copper oxide powder in a stable manner.

[0022]

In the present invention, it is preferable to use a nitrogen gas or an argon gas as the carrier gas suitable for supplying the copper oxide powder from the copper oxide powder supply equipment via the supply tube having an ability to remove static electricity. When a nitrogen gas or an argon gas is used, aggregation of copper oxide powder is suppressed, and hence it is possible to reliably reduce the adhesion of copper oxide powder to the supply tube, and to reliably prevent clogging.

[0023]

In the insoluble-anode plating equipment of the present invention, it is preferable to provide a switching unit to the supply tube, the switching unit being capable of switching between supplying the carrier gas and the copper oxide powder and supplying only the carrier gas. When the supply of copper oxide powder is stopped, only the carrier gas is supplied to the supply tube, and hence aggregation of copper oxide powder in the supply tube is prevented. Accordingly, it is possible to reliably prevent the adhesion of copper oxide powder and clogging.

[0024]

In the insoluble-anode plating equipment of the present invention, it is preferable that the supply tube be provided with a powder supply control unit configured to control adjustment of a supply amount of the copper oxide powder and stopping of supply of the copper oxide powder, a powder flowmeter being disposed in the powder supply control unit, and being configured to monitor a supply status of the copper oxide powder. By monitoring a supply status with the powder flowmeter, it is possible to appropriately perform fine adjustment of the supply amount of copper oxide powder or stopping of supply of the copper oxide powder when an abnormality occurs. In addition, it is preferable that, as a means for confirming sure adjustment of the copper concentration in the copper plating solution, copper densitometers be assembled onto upstream and downstream pipings of the copper concentration adjustment tank to monitor whether copper is accurately replenished for copper used in the plating process.

[0025]

In the insoluble-anode plating equipment of the present invention, to prevent the different solutions respectively supplied to the lower anolyte chamber and the upper catholyte chamber from directly mixing with each

other, it is preferable that a silicon ring be firmly fixed to each of the outer peripheral end of the separating membrane and the hole edge of the through-hole of the separating membrane. In the case where the silicon ring is firmly fixed to the separating membrane, it is preferable to use a process called simultaneous casting of the silicon ring. The simultaneous casting of the silicon ring is performed in the following manner. The separating membrane is fixed to a molding box that can push: the outer peripheral end of the separating membrane having the through-hole provided in the center thereof; and the hole edge of the through-hole, from above and below. An adhesive (primer) is applied to the outer peripheral end portion and the hole edge portion to each of which the silicon ring is to be firmly fixed. Silicon is injected into the portions to which the adhesive has been applied. Then, the molding box is pressurized. After the silicon is cured, when the molding box is removed, the silicon ring is firmly fixed to each of the outer peripheral end of the separating membrane and the hole edge of the through-hole of the separating membrane. With the use of the separating membrane to which such a silicon ring as described above is firmly fixed, it is possible to reliably prevent solution leakage from: the portion of the separating membrane outer peripheral end fixed to the plating tank inner wall; and the portion of the hole peripheral end of the through-hole in the separating membrane center, the portion of the hole peripheral end being fixed to the solution supply piping. The material of the separating membrane to be used is not particularly limited, and may be selected in consideration of solution permeability and resistance to the plating solution. It is preferable to use a separating membrane whose separating membrane base material is a polyethylene terephthalate resin and whose separating membrane material is a polyvinylidene fluoride resin-based material. Moreover, it is preferable that the water permeability be equal to or less than 0.1 mL/min/cm^2.

[0026]

Although the insoluble-anode plating equipment of the present invention is used for a copper plating process, provided that plating metal or plating solution components can be supplied in the form of powder in a plating process, the insoluble-anode plating equipment of the present invention can also be used for such a plating process. For example, in the case where a non-cyanide gold plating process containing gold sulfite is performed, the insoluble-anode plating equipment of the present invention can be used for supplying sulfite powder to replenish sulfurous acid consumed due to the plating process. The insoluble-anode plating equipment of the present invention can also be used for, for example, an electrolytic nickel plating process that uses an insoluble anode.

[Advantageous Effects of Invention]

[0027]

The present invention allows the copper concentration in the cathode plating solution to be continuously maintained within a predetermined range in the insoluble-anode plating equipment in which the separating membrane is disposed. Accordingly, the consumption of additives contained in the cathode plating solution can be suppressed, and a favorable copper plating process can be uniformly and continuously performed on fine vias, fine trenches, or the like with a high aspect ratio.

BRIEF DESCRIPTION OF THE DRAWINGS

[0028]

Fig. 1 is a schematic cross-sectional view of an insoluble-anode plating equipment of a present embodiment;

Fig. 2 is a schematic cross-sectional view of a plating tank of the insoluble-anode plating equipment of the present embodiment;

Fig. 3 is a schematic cross-sectional view of the insoluble-anode plating equipment that includes a copper concentration adjustment tank of the present embodiment;

Fig. 4 is an SEM observation photograph of copper oxide powder A;

Fig. 5 is an SEM observation photograph of copper oxide powder B; and

Fig. 6 is an observation photograph of cross section of a via that is subjected to copper fill plating.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0029]

An embodiment of the present invention will be described with reference to drawings. Fig. 1 shows a schematic cross-sectional view of an insoluble-anode plating equipment of the present embodiment, and Fig. 2 shows the schematic cross section of a plating tank.

[0030]

The insoluble-anode plating equipment shown in Fig. 1 is constituted of a plating tank 1, a control tank 2, and an anode solution tank 3. A copper oxide powder supplier 4 is disposed in the vicinity of the control tank 3.

[0031]

First, the plating tank 1 shown in Fig. 1 will be described with reference to Fig. 2. A torus-shape separating membrane 11 having a through-hole in the center thereof is set in the plating tank 1. This separating membrane 11 has a separating membrane outer peripheral end fixed to a plating tank inner wall 12, and a hole peripheral end of the through-hole is fixed to a leading end of a solution supply piping 13, whereby the separating membrane 11 is inclined upward in the direction toward the outer periphery of the separating membrane 11 from the solution supply piping 13. An annular flow passage 14

is provided on the outer periphery of the solution supply piping 13. Moreover, a mesh-like insoluble anode 15 is disposed at the bottom part of the plating tank 1.

[0032]

When a wafer W as an object to be plated is placed in an opening part of the plating tank 1, an upper catholyte chamber U and a lower anolyte chamber D are formed in the plating tank 1. A cathode plating solution is supplied to the upper catholyte chamber U from the solution supply piping 13. An anode solution in the anode solution tank 3 is supplied to the lower anolyte chamber D from the annular flow passage 14.

[0033]

The cathode plating solution stored in the control tank 2 is supplied to the upper catholyte chamber U in the plating tank 1 from the solution supply piping 13, is discharged from the outer peripheral end side of the separating membrane 11, and then returns to the control tank 2. The copper oxide powder supplier 4 disposed in the vicinity of the control tank 1 is configured such that copper oxide powder in a powder storage compartment 41 is caused to pass through a supply tube 42 together with a carrier gas G, and is then supplied into the control tank 1 from a powder supply cylinder 43, which is attached to an upper lid body 21 of the control tank 1. The leading end of the powder supply cylinder 43 is disposed in the vicinity of the liquid surface of the cathode plating solution.

[0034]

The supply tube 42 of the copper oxide powder supplier 4 is provided with: a switching equipment 44, which is capable of switching between supplying carrier gas and copper oxide powder and supplying only carrier gas; and a powder supply control equipment 45, which is configured to control adjustment of the copper oxide powder supply amount and stopping

of supply of the copper oxide powder and includes a powder flowmeter configured to monitor a supply status of the copper oxide powder.

[0035]

Although an illustration is omitted, the control tank 2 is provided with a magnetic stirrer function as a liquid stirring unit, so that when copper oxide powder is supplied to the control tank 2, the copper oxide powder can be rapidly dissolved by stirring the solution. Although an illustration is omitted, a copper densitometer is also attached to the control tank 2 to allow constant measurement of the copper concentration in the cathode plating solution. The copper oxide powder supplier 4 is controlled such that when the copper concentration in the cathode plating solution falls below a set range due to the plating process, the copper oxide powder supplier 4 is actuated in response to a signal from the copper densitometer to supply a necessary amount of copper oxide powder to the control tank 2.

[0036]

Fig. 3 shows an insoluble-anode plating equipment that includes a copper concentration adjustment tank. A copper concentration adjustment tank 5 is configured to send the cathode plating solution with an adjusted copper concentration to the control tank 2, and configured to be capable of recovering the cathode plating solution in the control tank 2. The copper oxide powder supplier 4 is disposed in the vicinity of the copper concentration adjustment tank 5. In Fig. 3, the right side of a bold broken line represents the inside of a cleanroom, whereas the left side of the bold broken line represents the outside of the cleanroom. The copper concentration adjustment tank 5 and the copper oxide powder supplier 4 are disposed outside the cleanroom, and hence it is possible to reliably prevent contamination in the cleanroom caused with copper oxide powder.

[0037]

Although an illustration is omitted, the copper concentration adjustment tank 5 shown in Fig. 3 is provided with a magnetic stirrer function as a liquid stirring unit, so that when copper oxide powder is supplied to the copper concentration adjustment tank 5, the copper oxide powder can be rapidly dissolved by stirring the solution. Although an illustration is omitted, a copper densitometer is also attached to the copper concentration adjustment tank 5 to allow constant measurement of the copper concentration in the cathode plating solution. The copper oxide powder supplier 4 is controlled such that when the copper concentration in the cathode plating solution stored in the control tank 2 falls below a set range, the copper oxide powder supplier 4 is actuated in response to a signal from the copper densitometer, which is attached to the copper concentration adjustment tank 5, to supply a necessary amount of copper oxide powder to the copper concentration adjustment tank 5. The plating tank 1, the anode solution tank 3, and the copper oxide powder supplier 4 shown in Fig. 3 have substantially the same configurations as those described with reference to Fig. 1.

[0038]

<Solubility of copper oxide powder>

Next, the examination result for solubility of copper oxide powder in the present invention will be described. The following three types of copper oxide powder were used for evaluation.

Copper oxide powder A: average particle size 30 μm
(FCO-M6 made by FURUKAWA CHEMICALS CO., LTD.)

Copper oxide powder B: average particle size 3.7 μm
(FCO-500 made by FURUKAWA CHEMICALS CO., LTD.)

Copper oxide powder C: average particle size μm
(YS-808 made by Kunshan Deyang New Materials Technology Co., Ltd.)

[0039]

The respective copper oxide powders were measured for dissolution rate, packed bulk density, and angle of repose. Respective test conditions are as follows.

Dissolution rate: A copper sulfate solution (MF-Cu525 made by EEJA LTD.) was used as the plating solution, and a predetermined amount of copper oxide powder was added to a beaker into which 1L of the plating solution (solution temperature 22°C) is charged. Measurement was performed for the time required for the copper sulfate solution to turn from black back to the original color of the copper sulfate solution due to complete dissolution of the copper oxide powder, and for the copper concentration in the plating solution after the lapse of a predetermined time from the addition of the copper oxide powder. The dissolution amount was measured from the copper concentration before the copper oxide powder is added and the copper concentration after the lapse of a predetermined time from the addition of the copper oxide powder, and the dissolution rate of the copper oxide powder was measured from the time required for complete dissolution.

Packed bulk density: A 200 mL graduated cylinder was used. A small amount of copper oxide powder was added to the graduated cylinder, and the bottom part of the graduated cylinder was tapped on a desk three times to solidify the powder. This solidification operation was repeated to add the copper oxide powder until the copper oxide powder reaches 100 mL. The weight of the added copper oxide powder was measured to measure a packed bulk density.

Angle of repose: The above-mentioned copper oxide powder (100 mL), the packed bulk density of which was measured, and that is charged into the 200 mL graduated cylinder, was dropped onto the desk from a height of 15 cm to form a lump of copper oxide powder in a state of being piled in a mountain

shape, and the angle of the skirt of the mountain-shaped lump was then measured.

[0040]

The measurement results for the dissolution rates, the packed bulk densities, and the angle of repose of the respective copper oxide powders are shown in table 1.

[0041]

[Table 1]

	Dissolution rate (g/L)/min	Packed bulk density (g/cm^3)	Angle of repose (°)
Copper oxide powder A	4.267	1.6	12.5
Copper oxide powder B	0.005	2.23	22.5
Copper oxide powder C	1.76	1.22	15

[0042]

As shown in table 1, the copper oxide powder A had the highest dissolution rate value, and had a value for packed bulk density of 1.6. In contrast, the copper oxide powder B having the lowest dissolution rate had a value for packed bulk density of 2.23, and a value for angle of repose of 22.5, which is considered large. Although the copper oxide powder C had a result of a dissolution rate value being lower than that of the copper oxide powder A, the copper oxide powder C had a value for packed bulk density of 1.22, and a value for angle of repose of 15. From such results, it was found that when copper oxide powder has a packed bulk density of approximately 1.6 g/cm^3, and an angle of repose of approximately 12.5°, the copper oxide powder has a high dissolution rate.

[0043]

The results for SEM observation of particle shape and the measurement of specific surface area with respect to the copper oxide

powders A and B will be described. Fig. 4 shows an SEM observation photograph of the copper oxide powder A, and Fig. 5 shows an SEM observation photograph of the copper oxide powder B. In Fig. 4 and Fig. 5, an observation photograph at 1000 times magnification is shown on the upper side, and an observation photograph at 50000 times magnification is shown on the lower side. As shown in Fig. 4, when the copper oxide powder A was observed at 1000 times magnification, a large number of particles having a particle size of equal to or more than 20 μm were observed. In addition, when the copper oxide powder A was observed at 50000 times magnification, fine particles having a submicron particle size were observed over the entire field of view. As shown in Fig. 5, when the copper oxide powder B was observed at both 1000 times magnification and 50000 times magnification, a large number of particles having a particle size of 2 to 3 μm were observed. The specific surface area of the copper oxide powder B was 23 m^2/g, and the specific surface area of the copper oxide powder A was 0.8 m^2/g. Based on the results for the SEM observations and the measurements of specific surface areas, it can be understood that although the copper oxide powder A has an average particle size of 30 μm, which is considered a large value, a particle having this average particle size is formed due to aggregation of fine particles. It is deemed that the copper oxide powder A is a granular powder made of fine particles, thus having favorable fluidity of powder, and a relatively small angle of repose.

[0044]

<Copper plating test>

Next, results for a copper plating test will be described, a copper plating process using a copper sulfate plating solution being performed with the plating equipment of the present embodiment in the copper plating test. This copper plating test was carried out with the insoluble-anode plating

equipment described with reference to Fig. 1. Commercially available equipment (MX-750: made by Kinboshi Inc.) was adopted as the copper oxide powder supplier.

[0045]

This test was carried out in the following manner: a copper sulfate plating solution containing three types of additives (commercial products) called an accelerator (promotor), a suppressor (inhibitor), and a leveler (smoother) was supplied to the upper catholyte chamber corresponding to a cathode side; and a copper sulfate plating solution containing no additive was supplied to the lower anolyte chamber corresponding to an anode side. The solution compositions are shown below.

[0046]

*Solution Supplied to Upper Catholyte Chamber:

· Copper sulfate plating solution (commercial product MicroFab Cu525 / made by EEJA LTD.)

Copper concentration ··· 60 g/L

Sulfuric acid concentration ··· 30 g/L

· Accelerator 5W (promotor) ··· 3 mL/L

· Suppressor (inhibitor) ··· 10 mL/L

· Leveler (smoother) ··· 10 mL/L

· Solution temperature 22 to 23°C

· Solution volume 40 L

· Supply flow rate 25 L/min

*Solution Supplied to Lower Anolyte Chamber:

· Copper sulfate plating solution (commercial product MicroFab Cu525/ made by EEJA LTD., which is the same solution as that for the upper catholyte chamber)

· Solution temperature 22 to 25°C

· Solution volume 20 L

· Supply flow rate 5 L/min

[0047]

In the plating equipment, a mesh-like insoluble anode made of Pt-Ti was used, and a commercial product (film material: a fluorine-based resin, thickness: 0.12 mm, water permeability: 0.08 mL/min/ cm^2 25°C) was used as the separating membrane. An 8-inch wafer made of PCB was used as the object to be plated. This wafer made of PCB is an object to be plated that is a glass epoxy base material to which copper foil is attached and which is processed into a wafer-like circular shape.

[0048]

In this copper plating test, a running test, in which the copper plating process was performed and the copper oxide powder was supplied, was carried out, and changes in the concentration of the additives contained in the solution supplied to the upper catholyte chamber were examined. The above-described copper oxide powder A was used as the copper oxide powder, and nitrogen gas was used as the carrier gas. A supply tube made of PFA (tetrafluoroethylene·perfluoroalkylvinyl ether copolymer), and having an inner diameter of 1 mm, and an outer diameter of 2 mm was used, and a powder supply cylinder having an inner diameter of 20.4 mm, and an outer diameter of 25 mm was used. This powder supply cylinder was disposed such that the leading end (the end from which the copper oxide powder is blown out) of the powder supply cylinder is located approximately 80 mm above the surface of the plating solution in the control tank.

[0049]

Copper plating was performed under conditions that the plating current was supplied at an average current density of 0.91 A/dm^2 (plating time 44 min) to achieve an amount of precipitated Cu per wafer of 0.45 g. In addition,

a control was performed such that, when the copper plating process is performed on one wafer, 0.5625 g of the copper oxide powder A is supplied to the plating solution in the control tank with a nitrogen gas flow rate of 0.06 L/min (corresponding to the supply amount of the copper oxide powder A of 0.3 g/min). In the control tank to which the copper oxide powder A is supplied, the solution was stirred using a magnetic stirrer function.

[0050]

The copper plating process was sequentially performed on four wafers, and the plating solution in the upper catholyte chamber was collected to analyze the concentration of the additives after each plating process was performed. In addition, the copper concentration was also analyzed after each plating process was performed. As a result, it was confirmed that there is almost no fluctuation in the concentration of the three additives in the copper sulfate plating solution supplied to the upper catholyte chamber. Further, the copper concentration in the copper sulfate plating solution supplied to the upper catholyte chamber was held substantially constant. When the copper sulfate plating solution in the lower anolyte chamber was analyzed after each plating process was performed, the components of the three additives were not analyzed. From such results, it was confirmed that the additives in the copper sulfate plating solution in the upper catholyte chamber did not move to the lower anolyte chamber.

[0051]

Next, the result of a copper fill plating test for a via will be described. In this test, a Si wafer with a via having a diameter of 30 μm, and a depth of 70 μm was used. Copper was filled in this via, and a pad (Pad) having a thickness of 12 μm, and a diameter of 80 μm was continuously formed on the top of this via by performing copper plating. The copper sulfate plating solution and the copper oxide powder A that are used, other conditions of

equipment, and the like are substantially equivalent to those in the above-mentioned running test carried out for examining changes in the concentration of the additives.

[0052]

Before the copper fill plating was performed, a Si wafer was installed in a reduced pressure atmosphere and, thereafter, pickling and pure water cleaning were sequentially performed. Then, the copper fill plating was performed for the via. Plating conditions were as follows. An initial process was performed for 0.5 mi with a current density of 0.9 A/dm^2. A first process was performed for 19.5 min with a current density of 0.9 A/dm^2. A second process was performed for 14.6 min with a current density of 1.36 A/dm^2. The first process corresponds to filling of the via, and the second process corresponds to the copper plating process performed on the top of the via.

[0053]

Fig. 6 shows an observation photograph of the cross section of the via that is subjected to the copper fill plating. It was confirmed that the inside of the via is completely filled due to the copper plating. It was found that the copper fill plating can be reliably performed on the fine via having a diameter of 30 μm and a depth of 70 μm with the plating equipment of the present embodiment.

Reference Signs List

[0054]

1 plating tank

11 separating membrane

12 plating tank inner wall

13 solution supply piping

14 annular flow passage

15 insoluble anode

2 control tank

21 upper lid body

3 anode solution tank

4 copper oxide powder supplier

41 powder storage compartment

42 supply tube

43 powder supply cylinder

44 switching equipment

45 powder supply control equipment

5 copper concentration adjustment tank

51 upper lid body

U upper catholyte chamber

D lower catholyte chamber

W wafer

G carrier gas