ELECTROLESS COPPER PLATING BATH AND ELECTROLESS COPPER PLATING METHOD

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ABSTRACT

Provided are an electroless copper plating bath and an electroless copper plating method using the electroless copper plating bath, the electroless copper plating bath not containing formaldehyde; being usable under approximately neutral pH conditions; improving plating bath stability; and capable of forming a plating film with a good thickness while controlling deposition outside a pattern. The electroless copper plating bath according to the present invention contains a water-soluble copper salt; an amine borane or a substituted derivative thereof as a reducing agent; does not contain formaldehyde; and has a pH of 4 to 9, wherein polyaminopolysilphonic acid as a complexing agent, an anionic surfactant, an antimony compound, and a nitrogen-containing aromatic compound are contained.
FIG. 1

Deposition Film Thickness vs. Antimony Concentration

- Occurrence of Edge Thinning

- Concentration values (mg/L): 0, 5, 10, 15, 20, 25

- Film thickness values (µm/hr): 0, 2, 4, 6, 8, 12

[Graph showing the relationship between film thickness and antimony concentration.]
FIG. 2

DEPOSITION FILM THICKNESS [μm/hr]

ANTIMONY CONCENTRATION [mg/L]

OCCURRENCE OF EDGE THINNING
ELECTROLESS COPPER PLATING BATH AND ELECTROLESS COPPER PLATING METHOD

BACKGROUND OF THE INVENTION

[0001] Field of the Invention
[0002] The present invention relates to an electroleless copper plating bath and an electroleless copper plating method, more specifically, an electroleless copper plating bath not containing formaldehyde and being usable at approximately neutral pH, and an electroless copper plating method using the electroless copper plating bath.


[0004] Description of the Related Art
[0005] Formaldehyde has been used for a conventional electroless copper plating bath as a reducing agent for copper ions. However, the vapor pressure of formaldehyde is high, and deterioration of work environment by the irritating odor and harmful effects on the human body due to carcinogenicity have been pointed out. In addition, an electroless copper plating bath using formaldehyde is strongly alkaline, whereby a material to be plated is damaged and easily deteriorates, and thus the electrolese copper plating bath cannot be effectively used, for example, for metal, such as aluminum or aluminum alloy, and the use has been limited.

[0006] On the other hand, for example, as disclosed in Japanese Patent Laid-Open No. 2001-131761, an electroleless copper plating bath not containing formaldehyde as a reducing agent, but containing amine borane or a derivative thereof has been proposed. Amine borane is usable as a reducing agent under neutral to weakly alkaline pH conditions, thereby preventing deterioration of a material to be plated and being usable with high safety.

[0007] However, amine borane has a considerably high reducing power, and has a problem that a plating bath is easily decomposed. There has not been an electroleless copper plating bath solution containing amine borane as a reducing agent while having good bath stability and high practicality.

[0008] In the case where formaldehyde is used as a reducing agent, the formaldehyde shows a strong reduction power selectively over the surface of metal, such as palladium and copper, while has a weak reducing action in a plating bath, and therefore deposition does not take place easily on a portion other than a pattern (metal). On the other hand, a borane compound, such as dimethylamine borane, has a reducing power strong enough to reduce water to hydrogen, thereby reducing metal ions to metal not only on a metal but also in a plating bath, and therefore there has been a problem that the selectivity onto a pattern is low, and accordingly deposition takes place outside a pattern.


[0010] The present invention is proposed in view of such conventional actual circumstances, and the purpose of the present invention is to provide an electroless copper plating bath and an electroless copper plating method using the electroless copper plating bath, the electroless copper plating bath not containing formaldehyde, being usable under approximately neutral pH conditions; improving plating bath stability; and being capable of forming a plating film with a good thickness while controlling deposition outside a pattern.

SUMMARY OF THE INVENTION

[0011] The present inventors earnestly studied to achieve the above-mentioned purpose, and, as a result, found that, in a formaldehyde-free electroless copper plating bath, controlling the balance of promotion and inhibition of plating deposition enabled deposition outside a pattern to be effectively controlled while enabled a plating film with a good thickness to be formed, and completed the present invention.

[0012] In other words, an electroless copper plating bath according to the present invention is an electroless copper plating bath containing a water-soluble copper salt, and amine borane or a substituted derivative thereof as a reducing agent; not containing formaldehyde; and having a pH of 4 to 9, wherein polyanaminopolyphosphonic acid as a complexing agent, an anionic surfactant, a surfactant-containing compound, and a nitrogen-containing aromatic compound are contained.

[0013] An electroless copper plating method according to the present invention is characterized in that a copper plating film is formed on a substrate by using the above-mentioned electroless copper plating bath.

[0014] According to the present invention, the electroless copper plating bath can be used under approximately neutral pH conditions, and plating treatment can be performed for a material to be plated without causing damage. In addition, plating deposition outside a pattern can be effectively controlled, and a plating film with a good thickness can be formed. Thus, plating treatment is performed simply and easily without providing a barrier layer or the like for a base material made of aluminum, aluminum alloy, or the like, and the electroless copper plating bath can be suitably used for manufacturing of semiconductor wafers and the like.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] FIG. 1 is a graph showing a relationship between an antimony concentration in an electroless copper plating bath and a deposition film thickness.

[0016] FIG. 2 is a graph showing a relationship between an antimony concentration in an electroless copper plating bath and a deposition film thickness.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0017] A specific embodiment of an electroless copper plating bath and an electroless copper plating method according to the present invention (hereinafter, referred to as the present embodiment) will be described in detail in the following order.

[0018] 1. Electroless Copper Plating Bath

[0019] 2. Electroless Copper Plating Method

[0020] 3. Examples

1. ELECTROLESS COPPER PLATING BATH

[0021] The electroless copper plating bath according to the present embodiment is an electroless copper plating bath, not containing formaldehyde, that is, what is called a formaldehyde-free plating bath; containing a water-soluble copper salt, and amine borane or a substituted derivative thereof as a reducing agent; and having a pH of 4 to 9. The electroless copper plating bath is characterized in that
polyaminopolyphosphonic acid as a complexing agent, an anionic surface active agent, an antimony compound, and a nitrogen-containing aromatic compound are contained.

As mentioned above, the electroless copper plating bath according to the present embodiment does not contain a reducing agent, such as formaldehyde or glyoxylic acid, which is used under strongly alkaline pH conditions, but contains amine borane or a substituted derivative thereof as a reducing agent, which can be used under neutral to weakly alkaline pH conditions. Thus, unlike the case of a plating bath of strongly alkaline pH in which formaldehyde or the like is used as a reducing agent, a metal base material used as a material to be plated is not damaged. Therefore, the electroless copper plating bath according to the present embodiment can be suitably used, for example, as a plating bath to form a plating film for a semiconductor wafer made of aluminum, aluminum alloy, or the like, and can form a good plating film.

In the case where amine borane or a substituted derivative thereof is used as a reducing agent, there is a problem that, due to the very strong reducing power, a plating bath easily decomposes, and deposition outside a pattern formed on a base material to be plated is produced, and thus the pattern selectivity is low. However, the electroless copper plating bath according to the present embodiment contains polyaminopolyphosphonic acid as a complexing agent, an anionic surface active agent, an antimony compound, and a nitrogen-containing aromatic compound, as mentioned above, whereby stability of the plating bath can be increased and the balance of promotion and inhibition of plating deposition can be controlled, and, with a higher pattern selectivity, a plating film with a good thickness can be formed.

Such electroless copper plating bath can simply and easily form a good plating film having no plating protrusion on a metal base material, such as aluminum or aluminum alloy, or magnesium or magnesium alloy, without providing a barrier layer or the like thereon to prevent deposition outside a pattern, and can be suitably used, for example, in manufacturing of semiconductor wafers.

Examples of a water-soluble copper salt include copper sulfate, copper nitrate, copper chloride, copper acetate, copper citrate, copper tartrate, and copper gluconate, and these water-soluble copper salts may be used alone or two or more kinds of these may be mixed at an arbitrary ratio and used.

As a concentration of the water-soluble copper salt, for example, a copper concentration may be 0.005 to 0.5 mol/L, preferably 0.01 to 0.5 mol/L, more preferably 0.05 to 0.1 mol/L. When the concentration of the water-soluble copper salt is less than 0.005 mol/L, a deposition rate is slower and a plating time is longer, which is not economical. On the other hand, when the concentration exceeds 0.5 mol/L, an amount of pumping increases and a cost rises, and in addition, a plating solution is unstable. Furthermore, nodules and roughness are easily formed and pattern characteristics are lowered.

Examples of amine borane or a substituted derivative thereof as a reducing agent include dimethyamine borane, tert-butylamine borane, triethylamine borane, and trimethylamine borane.

Amine borane or a substituted derivative thereof is a reducing agent which is usable at neutral to weakly alkaline pH. Accordingly, amine borane or a substituted derivative thereof is not used for a plating bath having a strongly alkaline pH, such as a plating bath using an aldehyde reducing agent, such as formaldehyde and glyoxylic acid, and therefore damage to a metal base material or the like to be plated is controlled, and deterioration thereof can be prevented. In addition, unlike an aldehyde reducing agent, amine borane or a substituted derivative thereof can exclude deterioration of work environment and harmful effects on the human body, whereby safety can be improved.

A concentration of amine borane or a substituted derivative thereof as a reducing agent is preferably 0.01 to 0.5 mol/L.

<Complexing Agent>
The electroless copper plating bath according to the present embodiment contains polyaminopolyphosphonic acid as a complexing agent.

Polyaminopolyphosphonic acid can easily complex copper ions efficiently at approximately neutral pH, and control decomposition of a plating bath and improve the stability.

Specific examples of polyaminopolyphosphonic acid include N,N,N',N'-ethylenediaminetetraakis(methylene phosphonic acid), nitritoliris(methylene phosphonic acid), diethylenediamine penta(methylene phosphonic acid), diethylenetriamine penta(methylene phosphonic acid), bis(hexamethylenetriamine penta(methylene phosphonic acid)), and glycine N,N-bis(methylene phosphonic acid).

A concentration of polyaminopolyphosphonic acid as a complexing agent is not particularly limited, but preferably 0.01 to 1 mol/L. When the concentration is less than 0.01 mol/L, copper ions cannot fully be complexed and a plating bath could become unstable. On the other hand, when the concentration exceeds 1 mol/L, an amount of pumping increases and a cost rises. In addition, a deposition rate of copper is slower and a plating time is longer, which is not economical. Furthermore, a base film could be damaged and degraded.

<Anionic Surface Active Agent>
The electroless copper plating bath according to the present embodiment contains an anionic surface active agent. When an anionic surface active agent is made to be contained, stability of a plating bath can be improved.

A detailed mechanism which improves stability of a plating bath is not certain, but, it is presumed that, when an anionic surface active agent is added, the anionic surface active agent adsorbs to metal particles produced in a plating bath, thereby inhibiting the particles from further growing, and thus there is an effect that dissolution of the particles by the above-mentioned complexing agent and other additives is promoted. Furthermore, as a factor in improvement of bath stability, it also can be presumed that the dispersion effect by the anionic surface active agent inhibits the metal particles formed in a plating bath from agglomerating and growing.

On the other hand, adsorptivity of a cationic surface active agent to the surfaces of metal particles is too high, and therefore plating deposition is inhibited. Once a cationic surface active agent adsorbs to the surfaces, it is difficult to separate the cationic surface active agent from the surfaces. Compared with an anionic surface active agent or a cationic surface active agent, a nonionic surface active agent has lower adsorptivity to metal particles and lower effects in improving bath stability. The electroless copper plating bath has a high salt concentration, whereby a cloud point of a nonionic surface active agent is lowered and turbidity is easily produced. Furthermore, when a concentration of a nonionic surface
active agent is made high, the nonionic surface active agent has a high foaming property, whereby it becomes difficult to raise the concentration in order to improve bath stability.

[0041] Specific examples of the anionic surface active agent include an alkyl carboxylic acid surface active agent; naphthalene sulfonate formaldehyde condensate, such as sodium salt of α-naphthalenesulfonic formaldehyde condensate (for example, DEMOL N manufactured by Kao Corp.); and LAVELIN series manufactured by Dai-Ichi Kogyo Seiyaku Co., Ltd.); polyoxyalkylene ether sulfates, such as sodium polyoxyethylene lauryl ether sulfate (for example, EMAL 2G manufactured by Kao Corp.); and polyoxyethylene alkyl ether sulfates triethanolamine (for example, EMAL 201G manufactured by Kao Corp.); higher alcohol sulfates; and its salt, such as sodium dodecyl sulfate (for example, EMAL 10G manufactured by Kao triethanolamine dodecyl sulfate (for example, EMAL TD manufactured by Kao Corp.), and dodecyl ammonium sulfate (for example, EMAL AD-25 manufactured by Kao Corp.); alkylbenzene sulfonic acid or its salt, such as sodium dodecyl benzene sulfonate (for example, NEOPELEX GS manufactured by Kao Corp.); UPON LH-200 manufactured by Lion Corp., and MONOGEN Y-100 manufactured by Dai-Ichi Kogyo Seiyaku Co., Ltd.); and linear alkyl benzene sulfonate sodium (for example, NEOGEN S-20G manufactured by Dai-Ichi Kogyo Seiyaku Co., Ltd.). An alkyl sulfosuccinate ester surface active agent, such as sodium dodecyl sulfosuccinate (for example, PELEX OT-P manufactured by Kao Corp., ADEKA COL. EC-series manufactured by ADEKA Corp.), disodium lauryl sulfosuccinate (for example, NEOTENOL LS manufactured by Dai-Ichi Kogyo Seiyaku Co., Ltd.), and sodium dioctyl sulfosuccinate (for example, NEOCOL SW-C manufactured by Dai-Ichi Kogyo Seiyaku Co., Ltd.); polyoxyethylene alkyl sulfosuccinic acid or its salt (for example, NEOTENOL S-70 manufactured by Dai-Ichi Kogyo Seiyaku Co., Ltd.); monoalkyl phosphoric ester or its salt (for example, ADEKA COL PS/CS/TS-series manufactured by ADEKA Corp., and Phospholan series manufactured by Toho Chemical Industry Co., Ltd.); polyoxyethylene alkyl ether phosphoric acid or its salt, such as polyoxyethylene tridecyl ether phosphoric ester (for example, PLYSURF A212C manufactured by Dai-Ichi Kogyo Seiyaku Co., Ltd.), and polyoxyethylene lauryl ether phosphoric ester (for example, PLYSURF A2088 manufactured by Dai-Ichi Kogyo Seiyaku Co., Ltd.); and α-olefin sulfonic acid or its salt (for example, NEOTENAO-90 manufactured by Dai-Ichi Kogyo Seiyaku Co., Ltd.).

[0042] A concentration of the anionic surface active agent is not particularly limited, but preferably 0.01 to 2000 mg/L. When the concentration is less than 0.01 mg/L, an effect as a stabilizer is not fully obtained and a plating bath could become unstable. Furthermore, nodules and roughness are easily formed. On the other hand, when the concentration exceeds 2000 mg/L, a foaming property is too high. Furthermore, water washability in a downstream process falls, and treatment of waste liquid and waste water becomes difficult.

[0043] <Antimony Compound>

[0044] The electroless copper plating bath according to the present embodiment contains an antimony compound. Thus, when an antimony compound is added, an effect of promotion of plating deposition by underpotential deposition phenomenon and an effect of deposition inhibition by a catalyst poison effect accompanying adsorption of antimony are balanced, whereby an effect of improvement in deposition rate and an effect of inhibition of plating protrusion can be obtained.

[0045] Note that the underpotential deposition phenomenon means a phenomenon in which, at the time when an element (antimony) to be added is redissolved as an ion immediately after being reduced, electrons are emitted, whereby deposition of target metal (copper) is promoted, and thus metal deposits at an electric potential lower than a theoretically-calculated deposition potential.

[0046] Specifically, in antimony compounds, the influence of a concentration thereof on deposition rate of the plating metal can be expressed graphically as a curve protruding upward, in other words, in both cases where the concentration is too low and too high, a deposition rate is slower, and there is a concentration at which a deposition rate is maximum. Thus, it is presumed that the inhibition appears at a pattern end portion (edge portion) to which antimony easily adsorbs, while, mainly the promotion appears at portions, other than the edge portion, to which antimony hardly adsorbs, whereby, even if a deposition rate is high, spread of plating deposition outside a pattern can be controlled.

[0047] Here, a relationship between a deposition rate of plating metal and a concentration of an antimony compound will be specifically explained with reference to specific experiment examples.

[0048] First, in Experiment Example 1, a sample was obtained in such manner that, on an Al—Si alloy sputtered film formed on a silicon wafer, a pattern was formed with a TiN film, and then a double zinicate treatment was performed in accordance with the usual method, and the sample was immersed in an electroless copper plating bath having the following composition for 1 hour to perform electroless copper plating treatment, whereby a copper plating film was formed on the pattern.

[0049] (Composition of Electroless Copper Plating Bath)

[0050] Ethylene diamine tetra(methylene phosphonic acid): 0.08 mol/L

[0051] Copper (copper sulfate pentahydrate): 0.063 mol/L (4 g/L as a copper concentration)

[0052] Dimethylamine borane: 8 g/L

[0053] Sodium lauryl sulfate: 20 mg/L

[0054] o-Phenanthroline: 4 mg/L

[0055] Antimony oxide: refer to Table 1 below. (as an antimony concentration)

[0056] pH: 7.7

[0057] Bath temperature: 60 degrees C.

[0058] Then, a film thickness of the formed plating film, an amount of deposition outside the pattern (a protrusion amount), and plating appearance were examined. Table 1 below shows each measurement result. FIG. 1 shows variations of deposition film thickness with respect to a concentration of antimony in the electroless copper plating bath. Note that, in Table 1 below, “bridge” in the evaluation of plating protrusion represents a state in which patterns are connected each other by plating protrusion, while “occurrence of edge thinning” in the evaluation of appearance represents a phenomenon in which a film thickness of a periphery portion of a substrate/pad is thinner. Note that a minus value of plating protrusion represents a state in which plating does not deposit at a pattern edge portion due to occurrence of edge thinning, whereby the base is exposed.
TABLE 1

<table>
<thead>
<tr>
<th>Antimony Concentration [mg/L]</th>
<th>Deposition Film Thickness [um/hrs]</th>
<th>Plating Protrusion [um]</th>
<th>Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.9</td>
<td>Bridge</td>
<td>Normal</td>
</tr>
<tr>
<td>1</td>
<td>4.7</td>
<td>20</td>
<td>Normal</td>
</tr>
<tr>
<td>2</td>
<td>5.3</td>
<td>5</td>
<td>Normal</td>
</tr>
<tr>
<td>3</td>
<td>5.9</td>
<td>5</td>
<td>Normal</td>
</tr>
<tr>
<td>4</td>
<td>9.4</td>
<td>0</td>
<td>Occurrence of Edge Thinning</td>
</tr>
<tr>
<td>5</td>
<td>7.5</td>
<td>-10</td>
<td>Occurrence of Edge Thinning</td>
</tr>
<tr>
<td>10</td>
<td>6.8</td>
<td>-15</td>
<td>Occurrence of Edge Thinning</td>
</tr>
<tr>
<td>20</td>
<td>No Deposition</td>
<td>No Deposition</td>
<td>No Deposition</td>
</tr>
</tbody>
</table>

[0059] It is understood that, when plating treatment is performed under the above-mentioned conditions of the plating bath composition and the base in Experiment Example 1, as shown in Table 1, in the cases of no addition and a lower concentration of antimony and a higher concentration of antimony, a plating deposition rate is lower, and a plating film thickness is thinner when abnormalities in deposition at a pattern edge portion are caused. On the other hand, it is understood that, when an antimony concentration is in the approximately middle of a concentration range shown in Table 1, a plating film with a good thickness is formed, and spread of plating deposition outside a pattern and occurrence of edge thinning are controlled.

[0060] Next, in Experiment Example 2, a sample was obtained in such a manner that, in accordance with the usual method, a palladium substitution treatment was performed for a ceramic substrate on which a pattern was formed with a nickel film, and the sample was immersed in an electroless copper plating bath having the same composition as in Experiment Example 1 for 1 hour to perform an electroless copper plating treatment, whereby a copper plating film was formed on the pattern. In other words, there was examined a relationship between a deposition rate of plating metal and a concentration of an antimony compound in the case of changing conditions of the base for which plating treatment is to be given. Note that a concentration of antimony oxide which was one of compositions of the plating bath (as an antimony concentration) was changed as shown in Table 2 below.

[0061] Then, a film thickness of the formed plating film, an amount of deposition outside the pattern (a protrusion amount), and plating appearance were examined. Table 2 below shows each measurement result. FIG. 2 shows variations of deposition film thickness with respect to a concentration of antimony in the electroless copper plating bath. Note that terms used for the evaluation shown in Table 2 below represent the same as those used in Table 1 above.

TABLE 2

<table>
<thead>
<tr>
<th>Antimony Concentration [mg/L]</th>
<th>Deposition Film Thickness [um/hrs]</th>
<th>Plating Protrusion [um]</th>
<th>Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.8</td>
<td>Bridge</td>
<td>Normal</td>
</tr>
<tr>
<td>0.5</td>
<td>3.2</td>
<td>12</td>
<td>Normal</td>
</tr>
<tr>
<td>1</td>
<td>5.0</td>
<td>28</td>
<td>Normal</td>
</tr>
<tr>
<td>2</td>
<td>6.5</td>
<td>20</td>
<td>Normal</td>
</tr>
<tr>
<td>3</td>
<td>7.5</td>
<td>15</td>
<td>Normal</td>
</tr>
<tr>
<td>4</td>
<td>9.4</td>
<td>8</td>
<td>Normal</td>
</tr>
<tr>
<td>5</td>
<td>9.5</td>
<td>10</td>
<td>Normal</td>
</tr>
</tbody>
</table>

[0062] As shown in Table 2, it is understood that, also in the case of changing conditions of the base, both when antimony is not added and when a concentration of antimony is low or high, a plating deposition rate is slower, and a plating film thickness is thinner while abnormalities in deposition at a pattern edge portion are caused. On the other hand, it is understood that, when an antimony concentration is in the approximately middle of a concentration range shown in Table 2, a plating film with a good thickness is formed, and spread of plating deposition outside a pattern and occurrence of edge thinning are controlled.

[0063] As shown in Experiment Examples 1 and 2 mentioned above, it is clearly understood that, although depending on conditions of a plating bath composition and a plating base, stirring conditions, and the like, a deposition rate is slower in both cases where an antimony concentration is too low and too high, and there is a concentration range in which a plating deposition rate is maximum. And it is understood that, in the concentration range in which a plating deposition rate is maximum, the inhibition of plating deposition appears at a pattern end portion (edge portion) to which antimony easily adsorbs, while mainly the promotion of plating deposition appears at portions other than a pattern edge portion, to which antimony hardly adsorbs, whereby a plating film with good thickness is formed while spread (plating protrusion) of plating deposition outside a pattern can be controlled.

[0064] Therefore, by thus adding a predetermined concentration of an antimony compound to a plating bath, an effect of improvement in a deposition rate and an effect of inhibition of plating protrusion can be obtained based on the balance between an effect of promotion of plating deposition and an effect of deposition inhibition by a catalyst poison effect accompanying adsorption of antimony, whereby pattern selectivity can be increased, and a plating film with a good film thickness in which plating protrusion is controlled can be formed.

[0065] As mentioned above, a specific amount (concentration) of an antimony compound added is different depending on conditions of other composition components of plating bath (plating composition) and a base, stirring conditions, and the like, thereby being preferably suitably changed in accordance with the conditions, but, for example, may be 0.1 to 20 mg/L, preferably 0.5 to 10 mg/L, more preferably 1 to 4 mg/L.

[0066] The antimony compound is not limited so far as it is a water-soluble compound which dissolves in a plating bath, and for example, antimony oxide, antimony chloride, and the like may be used.

[0067] ＜Nitrogen-Containing Aromatic Compound＞

[0068] The electroless copper plating bath according to the present embodiment contains a nitrogen-containing aromatic compound.
Conventionally, a nitrogen-containing aromatic compound, such as example 2,2'-bipyridyl and 1,10-phenanthroline, has been used as a stabilizer or an agent to improve film physical properties of a plating bath. However, although a detailed mechanism is not certain, when a nitrogen-containing aromatic compound is added to the electroless copper plating bath according to the present embodiment, the nitrogen-containing aromatic compound comes to act as a promoter which promotes metal plating.

Specific examples of the nitrogen-containing aromatic compound include imidazole or a substituted derivative thereof; pyrazole or a substituted derivative thereof; oxazole or a substituted derivative thereof; thiazole or a substituted derivative thereof; pyridine or a substituted derivative thereof; pyrazine or a substituted derivative thereof; pyrimidine or a substituted derivative thereof; pyridazine or a substituted derivative thereof; triazine or a substituted derivative thereof; benzothiophene or a substituted derivative thereof; benzoazainole or a substituted derivative thereof; pyridine or a substituted derivative thereof; such as 2,2'-dipyridyl, 4,4'-dipyridyl, nicotinic acid, nicotinamide, picoline, or lutidine; quinoline or a substituted derivative thereof; such as hydroxyquinoline; acridine or a substituted derivative thereof; such as 3,6-dimethylaminocaridine, proflavine, acridine acid, or quinoline-1,2-dicarboxylic acid; pyrimidine or a substituted derivative thereof, such as uracil, uridine, thymine, 2-thiouracil, 6-methyl-2-thiouracil, or 6-propyl-2-thiouracil; phenanthroline or a substituted derivative thereof; such as 1,10-phenanthroline, neocuproine, or bathophenanthroline; and purine or a substituted derivative thereof; such as aninopurine, adenine, adenosine, guanine, hydantoin, adenine, xanthine, hypoxanthine, caffeine, theophylline, theobromine, or aminophylline.

A concentration of the nitrogen-containing aromatic compound is not limited, but preferably 0.01 to 1000 mg/L. When the concentration is less than 0.01 mg/L, an effect as a promoter is not obtained, and a deposition rate is slower and a plating time is longer, which is not economical. Furthermore, deposition of copper at an initial stage is poorer, whereby a base material could be damaged and an undeposited portion could be produced. On the other hand, when the concentration exceeds 1000 mg/L, a deposition rate is too high, so that a rough film is produced. In addition, nodules and roughness are easily formed, and pattern characteristics are lowered. Furthermore, a plating bath could become unstable.

The plating bath has a pH of 4.0 to 9.0, preferably a pH of 5.0 to 9.0, more preferably a pH of 6.0 to 8.0. As mentioned above, the electroless copper plating bath according to the present embodiment contains, as a reducing agent, amine borane or a substituted derivative thereof, which is usable under neutral to alkaline pH conditions. Thus, the electroless copper plating bath can be used in a range of pH 4.0 to pH 9.0, and plating treatment can be performed without giving damage to a base material to be plated.

Here, when the pH is less than 4.0, natural consumption of the reducing agent increases, thereby leading to an increase in cost, and the plating bath becomes unstable. On the other hand, when the pH is more than 9.0, damage to the base material to be plated increases.

The pH of the plating bath can be adjusted, for example, by making a pH adjustor, such as sodium hydroxide, potassium hydroxide, or tetramethyl ammonium hydroxide, contained.

A temperature of the plating bath is not particularly limited, but 20 to 90 degrees C., preferably 40 to 80 degrees C., more preferably 60 to 70 degrees C. When the bath temperature is less than 20 degrees C., a deposition rate is slower and a plating time is longer, which is not economical. On the other hand, when the bath temperature exceeds 90 degrees C., a deposition rate is too high, so that a rough film is produced, and in addition, a warp of a base material sometimes occurs due to heat shrinkage of a film after plating. In addition, nodules and roughness are easily formed, and pattern characteristics are lowered. Furthermore, a plating bath could become unstable, and natural consumption of a reducing agent increases, thereby leading to an increase in cost.

As mentioned above, the electroless copper plating bath according to the present embodiment is an electroless copper plating bath containing amine borane or a substituted derivative thereof as a reducing agent, and not containing formaldehyde, wherein polyaminopolysilphonic acid as a complexing agent, an anionic surface active agent, an antimony compound, and a nitrogen-containing aromatic compound are contained. This electroless copper plating bath is usable at approximately neutral pH, and therefore, without giving damage to a material to be plated, good plating treatment can be performed, for example, for a material to be plated which easily deteriorates, such as aluminum.

Furthermore, the electroless copper plating bath can improve the stability of the plating bath, and also can control the balance between promotion and inhibition of plating deposition, thereby effectively controlling the plating protrusion outside a pattern while not making a thinner edge and the like occur, and a desired plating film with a good thickness can be formed.

Thus, for example, a good plating film without plating protrusion can be simply and easily formed on aluminum or aluminum alloy, or magnesium or magnesium alloy, without providing a barrier layer or the like to prevent deposition outside a pattern, and the electroless copper plating bath can be suitably used, for example, in manufacturing of semiconductor wafers.

Furthermore, as mentioned above, since the balance between promotion and inhibition of plating deposition can be controlled, a plating film to be formed is smooth, for example, peel strength of wire bonding can be improved. Moreover, the appearance of the plating film is excellent.

2. ELECTROLESS COPPER PLATING METHOD

Next, an electroless copper plating method using the above-mentioned electroless copper plating bath will be explained. A well-known method may be used as the electroless copper plating method. Also, in the case where catalyst addition treatment or the like is required as pretreatment, a well-known method may be applied as the catalyst addition treatment.

When electroless copper plating treatment is performed, as mentioned above, a bath temperature of the electroless copper plating bath is controlled to be 20 to 90 degrees C., preferably 40 to 80 degrees C., more preferably 60 to 70 degrees C.

Electroless copper plating treatment time is not particularly limited, and may be suitably set so as to obtain a
desired film thickness. Specifically, the time may be, for example, approximately 30 seconds to 15 hours.

[0084] When the electrolecless copper plating treatment is performed, as the plating treatment progresses, copper ions are reduced to copper metal by a reducing agent and deposit on a base material, and as a result, a concentration of copper ions and a concentration of a reducing agent in a plating solution decrease, and the pH of the plating solution also varies. Therefore, it is preferable that a water-soluble copper salt as a source of copper ions, a reducing agent, a complexing agent, and other additives are supplied into the electrolecless copper plating solution continuously or periodically to maintain those concentrations in a predetermined concentration range.

[0085] Moreover, the electrolecless copper plating bath is preferably stirred by air bubbling or the like, as needed.

[0086] Specifically, the electrolecless copper plating method using the electrolecless copper plating bath is such that, for example, without providing a barrier layer, zincte treatment (zinc substitution) is performed for a base material made of aluminum or aluminum alloy, or magnesium or magnesium alloy, and then electrolecless copper plating treatment is performed using the above-mentioned electrolecless copper plating bath. By the electrolecless copper plating method according to the present embodiment, deposition outside a pattern can be controlled effectively as mentioned above, and therefore a good plating film can be formed simply and easily without providing a barrier layer or the like.

[0087] Another example of the electrolecless copper plating method is such that activation treatment is performed for a thin film containing copper, nickel, palladium, platinum, tungsten, molybdenum, rhodium, titanium, tantalum, and the like, by substitution for palladium, platinum, copper, and the like, and then, electrolecless copper plating treatment is performed using the above-mentioned electrolecless copper plating bath.

[0088] Another example of the electrolecless copper plating method is such that, after the above-mentioned activation treatment, reduction treatment is performed by a treatment solution containing borane or a substituted derivative thereof, and then electrolecless copper plating treatment is performed using the above-mentioned electrolecless copper plating bath.

3. EXAMPLES

[0089] Hereinafter, specific Examples according to the present invention will be described. Note that the present invention is not limited to any of the following Examples.

[0090] <Examination of Composition of Electrolecless Copper Plating Bath>

[0091] First, in Example 1 to Example 2, and Comparative Example 1 to Comparative Example 10, which are shown below, a film thickness of a plating film and a deposition amount outside a pattern (a plating protrusion amount) were examined by changing the composition of an electrolecless plating bath.

**Example 1**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium laurel sulfate</td>
<td>20 mg/L</td>
</tr>
<tr>
<td>o-phenanthroline</td>
<td>4 mg/L</td>
</tr>
<tr>
<td>Antimony oxide</td>
<td>2 mg/L as an antimony concentration</td>
</tr>
<tr>
<td>pH</td>
<td>7.7</td>
</tr>
<tr>
<td>Bath temperature</td>
<td>60 degrees C.</td>
</tr>
</tbody>
</table>

**Electrolecless Copper Plating Method**

[0092] A sample was obtained in such a manner that, on an Al—Si alloy sputtered film formed on a silicon wafer, a pattern was formed with a TiN film, and then double zincte treatment was performed in accordance with the usual method, and the sample was immersed in an electrolecless copper plating bath having the above-mentioned composition for 1 hour to perform electrolecless copper plating treatment, whereby a copper plating film was formed on the pattern.

[0103] (Evaluation)

[0104] For the formed plating film, difference in height between before and after the plating treatment was measured with a laser microscope to measure a plating film thickness. As a result, it was found that the formed plating film had a good film thickness, namely a film thickness of 5.3 μm, and there was almost no plating protrusion outside the pattern, namely 5 μm of plating protrusion.

**Example 2**

**Composition of Electrolecless Copper Plating Bath**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycine N,N-bis(methyleneephosphonic acid)</td>
<td>0.13 mol/L</td>
</tr>
<tr>
<td>Copper (copper sulfate pentahydrate)</td>
<td>0.063 mol/L (4 g/L as a copper concentration)</td>
</tr>
<tr>
<td>Dimethylamine borane</td>
<td>8 g/L</td>
</tr>
<tr>
<td>Sodium laurel sulfate</td>
<td>20 mg/L</td>
</tr>
<tr>
<td>2,9-dimethyl-1,10-phenanthroline</td>
<td>2 mg/L</td>
</tr>
<tr>
<td>Antimony oxide</td>
<td>2 mg/L as an antimony concentration</td>
</tr>
<tr>
<td>pH</td>
<td>7.7</td>
</tr>
<tr>
<td>Bath temperature</td>
<td>60 degrees C.</td>
</tr>
</tbody>
</table>

**Electrolecless Copper Plating Method**

[0115] A sample was obtained in such a manner that, on an Al—Si alloy sputtered film formed on a silicon wafer, a pattern was formed with a TiN film, and then double zincte treatment was performed in accordance with the usual method, and the sample was immersed in an electrolecless copper plating bath having the above-mentioned composition for 1 hour to perform electrolecless copper plating treatment, whereby a copper plating film was formed on the pattern.

**Example 3**

**Composition of Electrolecless Copper Plating Bath**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene diamine tetra(methylene phosphonic acid)</td>
<td>0.08 mol/L</td>
</tr>
<tr>
<td>Copper (copper sulfate pentahydrate)</td>
<td>0.063 mol/L (4 g/L as a copper concentration)</td>
</tr>
<tr>
<td>Dimethylamine borane</td>
<td>8 g/L</td>
</tr>
<tr>
<td>Sodium laurel sulfate</td>
<td>20 mg/L</td>
</tr>
<tr>
<td>o-phenanthroline</td>
<td>4 mg/L</td>
</tr>
<tr>
<td>Antimony oxide</td>
<td>2 mg/L as an antimony concentration</td>
</tr>
<tr>
<td>pH</td>
<td>7.7</td>
</tr>
<tr>
<td>Bath temperature</td>
<td>60 degrees C.</td>
</tr>
</tbody>
</table>

**Electrolecless Copper Plating Method**

[0116] For the formed plating film, difference in height between before and after the plating treatment was measured with a laser microscope to measure a plating film thickness. As a result, it was found that the formed plating film had a good film thickness, namely a film thickness of 5.3 μm, and there was almost no plating protrusion outside the pattern, namely 5 μm of plating protrusion.
an amount of plating protrusion outside the pattern was 15 μm. Thus, plating deposition was inhibited while a large amount of protruding deposition was produced, and accordingly pattern selectivity was very low.

Comparative Example 2

[0120] Electroless copper plating treatment was performed to form a copper plating film on a pattern in the same manner as in Example 1, except that 2 mg/L of lead was added in place of 2 mg/L of antimony in the composition of the electroless copper plating bath.
[0121] As a result, the formed plating film had a thickness of 2.2 μm and was thinner than those of Examples 1 and 2, and an amount of plating protrusion outside the pattern was 12 μm. Thus, plating deposition was inhibited while a large amount of protruding deposition was produced, and accordingly pattern selectivity was very low.

Comparative Example 3

[0122] Electroless copper plating treatment was performed to form a copper plating film on a pattern in the same manner as in Example 1, except that 0.3 mg/L of thallium was added in place of 2 mg/L of antimony in the composition of the electroless copper plating bath.
[0123] As a result, the formed plating film had a thickness of 1.8 μm and was considerably thinner than those of Examples 1 and 2. In addition, there was a large amount of plating protrusion outside the pattern, and the plating protrusion caused a connection between patterns (bridge), and therefore the amount of the plating protrusion could not be measured. Thus, plating deposition was inhibited while a large amount of protruding deposition was produced, and accordingly pattern selectivity was very low.

Comparative Example 4

[0124] Electroless copper plating treatment was performed to form a copper plating film on a pattern in the same manner as in Example 1, except that sodium lauryl sulfate was not contained in the composition of the electroless copper plating bath.
[0125] In Comparative Example 4, the plating bath decomposed during the plating treatment, whereby the plating treatment was not performed properly.

Comparative Example 5

[0126] Electroless copper plating treatment was performed to form a copper plating film on a pattern in the same manner as in Example 1, except that o-phenanthroline was not contained in the composition of the electroless copper plating bath.
[0127] As a result, although an amount of plating protrusion outside the pattern was small, namely 0.5 μm, a plating film thickness was considerably thinner, namely 1.2 μm, and a plating rate remarkably decreased.

Comparative Example 6

[0128] Electroless copper plating treatment was performed to form a copper plating film on a pattern in the same manner as in Example 1, except that 0.5 g/L of polyethylene glycol (PEG) #1000 was added in place of 20 mg/L of sodium lauryl sulfate in the composition of the electroless copper plating bath.
[0129] In Comparative Example 6, the plating bath decomposed during the plating treatment, whereby the plating treatment was not performed properly.

Comparative Example 7

[0130] Electroless copper plating treatment was performed to form a copper plating film on a pattern in the same manner as in Example 1, except that 2 mg/L of bismuth was added in place of 2 mg/L of antimony in the composition of the electroless copper plating bath.
[0131] As a result, the formed plating film had a good film thickness, namely a film thickness of 4.4 μm, but, due to plating protrusion outside the pattern, a connection between patterns (bridge) was produced, and therefore an amount of the plating protrusion could not be measured.

Comparative Example 8

[0132] Electroless copper plating treatment was performed to form a copper plating film on a pattern in the same manner as in Example 1, except that 0.08 mol/L of diethylene diamine pentaaacetic acid was added in place of 0.08 mol/L of ethylene diamine tetra(methylene phosphonic acid) in the composition of the electroless copper plating bath.
[0133] In Comparative Example 8, copper plating was not deposited, and corrosion of the Al—Si alloy sputtered film constituting the pattern occurred.

Comparative Example 9

[0134] Electroless copper plating treatment was performed to form a copper plating film on a pattern in the same manner as in Example 1, except that an electroless copper plating bath having the following composition was used.
[0135] (Composition of Electroless Copper Plating Bath)
[0136] Ethylene diamine tetraacetic acid: 0.08 mol/L
[0137] Copper (copper sulfate pentahydrate): 0.0315 mol/L (2 g/L as a copper concentration)
[0138] Formaldehyde: 2 g/L
[0139] Polyethylene glycol (PEG) #1000: 1 g/L
[0140] 2,2'-dipyridyl: 20 mg/L
[0141] pH: 13.2 (adjusted with NaOH)
[0142] Bath temperature: 60 degrees C.
[0143] In Comparative Example 9, the Al—Si alloy sputtered film dissolved, whereby the plating treatment was not performed properly. This is considered because the plating bath contained formaldehyde as a reducing agent, which was highly alkaline, thereby causing serious damage to a base material.

Comparative Example 10

[0144] Electroless copper plating treatment was performed to form a copper plating film on a pattern in the same manner as in Example 1, except that an electroless copper plating bath having the following composition was used.
[0145] (Composition of Electroless Copper Plating Bath)
[0146] Ethylene diamine tetraacetic acid: 0.08 mol/L
[0147] Copper (copper sulfate pentahydrate): 0.0315 mol/L (2 g/L as a copper concentration)
[0148] Glyoxylic acid: 6 g/L
[0149] Polyethylene glycol (PEG) #1000: 1 g/L
[0150] 2,2'-dipyridyl: 20 mg/L
[0151] pH: 13.2 (adjusted with NaOH)
[0152] Bath temperature: 60 degrees C.
In Comparative Example 10, the Al—Si alloy sputtered film dissolved, whereby the plating treatment was not performed properly. This is considered because the plating bath contained glyoxylic acid as a reducing agent, which was highly alkaline, as is the case with formaldehyde, thereby causing serious damage to a base material.

What is claimed is:

1. An electroless copper plating bath, comprising a water-soluble copper salt, and amine borane or a substituted derivative thereof as a reducing agent;
   not comprising formaldehyde; and having a pH of 4 to 9,
   wherein polyaminopolyphosphonic acid as a complexing agent, an anionic surface active agent, an antimony compound, and a nitrogen-containing aromatic compound are comprised.

2. The electroless copper plating bath according to claim 1, wherein a concentration of the polyaminopolyphosphonic acid is 0.01 to 1 mol/L.

3. The electroless copper plating bath according to claim 1, wherein a concentration of the anionic surface active agent is 0.01 to 2000 mg/L.

4. The electroless copper plating bath according to claim 1, wherein a concentration of the antimony compound is 0.1 to 20 mg/L.

5. The electroless copper plating bath according to claim 1, wherein a concentration of the nitrogen-containing aromatic compound is 0.01 to 1000 mg/L.

6. An electroless copper plating method, wherein a copper plating film is formed on a base material by using the electroless copper plating bath according to claim 1.

7. The electroless copper plating method according to claim 6, wherein the base material is made of aluminum or aluminum alloy, or magnesium or magnesium alloy.

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