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(54) **Additive for plating bath**

(57) A plating bath additive and a plating bath using the said additive are provided, which plating bath contains a hydroxyalkanesulfonic acid and which even when applied to an electronic part such as a semiconductor device does not give rise to a problem such as circuit-to-circuit insulation becoming defective. The plat-

ing bath additive contains a hydroxyalkanesulfonic acid as a main component and has an alkali metal content of less than 0.05 mass% relative to the hydroxyalkanesulfonic acid. The plating bath incorporates the said additive therein.

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DescriptionField of the Invention

[0001] The present invention relates to a plating bath additive containing a hydroxyalkanesulfonic acid as a main component, as well as a plating bath using the said additive.

Background of the Invention

[0002] Hydroxyalkanesulfonic acids have heretofore been used as a component of various plating baths. For example, in JP 53-14131A, a hydroxyalkanesulfonic acid is used as a plating bath component for the formation of tin-lead alloy electroplating so as to serve as a film for improving solderability or as an etching resist film.

[0003] In JP 11-1792A it is disclosed that a hydroxyalkanesulfonic acid is used as a plating bath component for plating to an electronic part or for forming Pb-Sn alloy salient electrodes onto a surface of a semiconductor wafer.

[0004] In JP 11-279787A it is disclosed that a hydroxyalkanesulfonic acid is used as a plating bath component for silver or silver alloy plating.

[0005] In JP 2000-87252A it is disclosed that a hydroxyalkanesulfonic acid is used as a plating bath component for an electroless tin-bismuth alloy plating bath.

[0006] However, for example isethionic acid as a conventional hydroxyalkanesulfonic acid is obtained as sodium salt by subjecting ethylene oxide to the action of sodium hydrogen sulfite (see Encyclopaedia Chimica, Vol. 1, page 581), which is then ion-exchanged to remove the alkali metal for use as an acid.

[0007] On the other hand, when plating an electronic part such as a semiconductor device in a plating bath containing a hydroxyalkanesulfonic acid, there sometimes has occurred a problem that circuit-to-circuit insulation in the electronic part is defective.

Summary of the Invention

[0008] Accordingly, it is an object of the present invention to provide a plating bath additive and a plating bath using the said additive, which plating bath contains a hydroxyalkanesulfonic acid and which even when applied to an electronic part such as a semiconductor device does not give rise to a problem such as circuit-to-circuit insulation becoming defective.

[0009] Having made earnest studies in view of the above-mentioned point, the present inventors found out that if an alkali metal was present within a plating bath, the alkali metal remained even if the surface of a plated article after plating was subjected to cleaning having such an economical characteristic as falling under an industrially allowable range, thus sometimes resulting in circuit-to-circuit insulation in the electronic part becoming defective. In this way we accomplished the present invention.

[0010] More specifically, the present invention resides in a plating bath additive containing a hydroxyalkanesulfonic acid as a main component, characterized in that the content of an alkali metal relative to the hydroxyalkanesulfonic acid is less than 0.05 mass%.

[0011] The present invention also resides in the above plating bath additive wherein the hydroxyalkanesulfonic acid is isethionic acid.

[0012] The present invention further resides in the above plating bath additive wherein the hydroxyalkanesulfonic acid is obtained by a method involving oxidizing a hydroxyalkylmercaptan with use of hydrogen peroxide.

[0013] The present invention further resides in a plating bath using the above additive.

[0014] According to the present invention there are provided a plating bath additive and a plating bath using the said additive, which plating bath contains a hydroxyalkanesulfonic acid and which even when applied to an electronic part such as a semiconductor device does not give rise to such a problem as circuit-to-circuit insulation in the electronic part becoming defective.

Detailed Description of Preferred Embodiments

[0015] The plating bath additive according to the present invention contains a hydroxyalkanesulfonic acid as a main component, with the content of an alkali metal relative to the hydroxyalkanesulfonic acid being less than 0.05 mass%.

[0016] The hydroxyalkanesulfonic acid component is not Specially limited. Compounds represented by the general formula HO-R-SO₃H are preferred wherein R is a hydrocarbon group having 1 to 12 carbon atoms and the hydroxyl group may be located at any position of R. Concrete examples are 2-hydroxyethane-1-sulfonic acid (isethionic acid), 2-hydroxypropane-1-sulfonic acid, 1-hydroxypropane-2-sulfonic acid, 3-hydroxypropane-1-sulfonic acid, 2-hydroxybutane-1-sulfonic acid, 4-hydroxybutane-1-sulfonic acid, 2-hydroxypentane-1-sulfonic acid, 2-hydroxyhexane-1-sulfon-

ic acid, and 2-hydroxydecane-1-sulfonic acid. Particularly, 2-hydroxyethane-1-sulfonic acid (isethionic acid) is preferred as the plating bath additive.

[0017] How to prepare the hydroxyalkanesulfonic acid is not specially limited. Reference will now be made to isethionic acid as an example. Isethionic acid can be obtained by a conventional method involving subjecting ethylene oxide to the action of sodium hydrogensulfite to afford sodium salt and subsequent ion exchange to remove an alkali metal component. In this case, the ion exchanging operation is repeated until the alkali metal content becomes less than 0.05 mass% relative to the hydroxyalkanesulfonic acid.

[0018] The method disclosed in JP 10-204052A, which involves oxidizing a hydroxyalkylmercaptan with use of hydrogen peroxide, is preferred because an alkali metal is not used and therefore a hydroxyalkanesulfonic acid with an alkali metal content of less than 0.05 mass% can be obtained more effectively.

[0019] The plating bath additive according to the present invention is useful as a hydroxyalkanesulfonic acid component added to the plating bath and the hydroxyalkanesulfonic acid content in the plating bath additive is arbitrary. Any other desired components than the hydroxyalkanesulfonic acid may be added into the plating bath of the present invention, provided it is necessary to make a control so that the alkali metal content relative to the hydroxyalkanesulfonic acid does not become 0.05 mass% or more.

[0020] Other components which may be added into the plating solution are not specially limited. As examples of such other components there are mentioned antioxidants (e.g., catechol, hydroquinone, ascorbic acid), brighteners or brightening aids (e.g., benzaldehyde, formalin, glyoxal), complexing agents (e.g., EDTA, ethylenediamine, citric acid), nonionic surfactants as homogenizers (e.g., polyethylene glycol, oxyethylene-oxypropylene block copolymer, alkyl-phenol ethylene oxide adducts, polyhydric alcohol fatty acid esters, fatty acid alkanol amides), and antioxidation aids or smoothing agents (e.g., thiourea, ethylene thiourea, thioglycolic acid).

[0021] The plating bath according to the present invention contains the plating bath additive described above. As other components than a hydroxyalkanesulfonic acid, components so far known as components of a plating bath containing a hydroxyalkanesulfonic acid may be used in respective known ranges.

Thus, arbitrary components may be selected for the plating bath of the invention as desired by a user, with no special limitation being placed thereon. As examples of such components, mention may be made of compounds (e.g., copper, tin, silver, and their salts and oxides, each alone or in combination of two or more) which supplies ions of a metal to be plated, inorganic acids, organic acids, oxidizing agents, reducing agents, surfactants, pH adjustors, pH controllers, buffer agents, smoothing agents, stress relaxation agents, stabilizers, complexing agents (chelating agents), brighteners, semibrighteners, antioxidants, dispersants, homogenizers, and other additives known to be incorporated in plating baths. Arbitrary components which may be incorporated in the plating bath additive of the present invention are also capable of being incorporated in the plating bath of the invention.

Examples

[0022] The present invention will be further described below by way of working Examples thereof, but it is to be understood that the present invention is not limited by the following Examples.

Example 1

[0023] 357 g (6.3 mol) of 60 mass% hydrogen peroxide was charged into a glass reactor equipped with an internal condenser, an agitator, a condenser having an opening/closing cock for solvent distillation, and a liquid introducing device, and thereafter 156 g (2.0 mol) of 2-mercaptoethanol was fed continuously from a liquid inlet at a rate of 0.4 mL/min under agitation. During this operation, the liquid temperature was held at 45°C by adjusting the amount of cooling water fed to the condenser. After the end of the addition of 2-mercaptoethanol, the agitation was continued at room temperature for 10 hours. Then, nitrogen gas was blown into the reaction solution through a sample inlet pipe and the reaction solution was held for 5 hours under heating at 110°C and at the atmospheric pressure, with agitation, while a portion of vapor was allowed to be discharged to the exterior of the reaction system. This reaction solution was then passed through a 35 mm dia. tower charged with 200 mL of an ion exchange resin (Duolite A-561, a product of Sumitomo Chemical Co.), from the top of the tower and is thereby purified to afford 54.0 mass% of an isethionic acid solution (yield 241.6 g : percent yield 95.9%). No alkali metal was detected from this aqueous isethionic acid solution (detection limit 10 ppb).

[0024] The aqueous isethionic acid solution was used as a plating bath additive (1).

Comparative Example 1 & Example 2

[0025] A 43 mass% aqueous solution of commercially available sodium isethionate (a product of Aoki Yushi Kogyo Co.) was prepared and was then passed through a 30 mm dia. tower charged with 82 mL of an ion exchange resin

(MONOSPHERIA 630C_H, a product of The Dow Chemical Co.), at a (downflow) SV1.0, from the top of the tower; and was thereby purified to afford 10 mass% of an aqueous isethionic acid solution having a sodium content of 5 mass% relative to isethionic acid. The aqueous isethionic acid solution was then concentrated to an isethionic acid concentration of 40 mass% and the thus-concentrated aqueous solution was used as a comparative plating bath additive (1).

[0026] After regeneration of the ion exchange resin by a conventional method, the same purifying operation as above was repeated twice for the comparative plating bath additive (1) to afford a 7.0 mass% aqueous isethionic acid solution having a sodium content of 0.03 mass%. This aqueous isethionic acid solution was then concentrated to 40 mass% to afford a plating bath additive (2) according to the present invention.

Example 3

[0027] A 49.2 mass% aqueous 2-hydroxypropane-1-sulfonic acid solution was prepared in the same way as in Example 1 except that 2-mercaptoethanol was substituted by 2-mercaptopropanol. No alkali metal was detected from the aqueous 2-hydroxypropane-1-sulfonic acid solution.

[0028] The aqueous 2-hydroxypropane-1-sulfonic acid solution thus prepared was used as a plating bath additive (3) according to the present invention.

Example 4 & Comparative Example 2

[0029] Using the plating bath additives prepared in Examples 1 to 3 according to the present invention and the comparative bath additive prepared in Comparative Example 1, aqueous solutions of the composition shown in Table 1 were prepared as plating baths (Sn plating baths).

Table 1

SnO	30 g/L
Thiourea	8 g/L
Additive for the plating baths (as hydroxyalkanesulfonic acid)	100 g/L
p-Cumylphenol ethylene oxide (1.0 mol) adduct	10 g/L
Glyoxazole	1 g/L
Catechol	1 g/L
Balance Water	

[0030] On the other hand, when two systems of adjacent copper circuits were formed on a silicon wafer and were each Sn-plated using each of the plating baths prepared above, then tested for circuit-to-circuit insulation. As a result, a satisfactory insulation was attained in case of using the plating baths prepared according to the present invention, but the insulation was poor in the case of the plating bath using the comparative plating bath additive prepared in Comparative Example 2.

Claims

1. A plating bath additive which comprises a hydroxyalkanesulfonic acid as main component, **characterized in that** the content of an alkali metal relative to the hydroxyalkanesulfonic acid is less than 0.05 mass%.
2. A plating bath additive according to Claim 1 wherein the hydroxyalkanesulfonic acid has the formula HO-R-SO₃H wherein R is a hydrocarbylene group and the hydroxyl group may be located at any position of R.
3. A plating bath additive according to Claim 1 or Claim 2, wherein the hydroxyalkanesulfonic acid is isethionic acid.
4. A plating bath additive according to any one of the preceding claims, wherein the hydroxyalkanesulfonic acid is preparable by oxidizing a hydroxyalkylmercaptan with use of hydrogen peroxide.
5. A plating bath containing the plating bath additive described in any of Claims 1 to 4.

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6. Use, as a plating bath additive, of a hydroxyalkanesulfonic acid as defined in any one of Claims 1 to 4 to improve the circuit-to-circuit insulation of product plated from the bath.

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