

[0108] The electric conductivity of the electrolytic liquid is preferably 5 to 200 mS/cm. When the electric conductivity of the electrolytic liquid is low, a higher voltage needs to be applied to carry out electrolytic polishing at an intended processing rate. The application of higher voltage will adversely affect electrolytic polishing, such as lowering of current efficiency in polishing due to the generation of oxygen, the formation of pits in a processed surface, lower flattening effect due to breakage of a protective film, etc. Thus, electrolytic polishing is desirably carried out at a low voltage. To this end, the electric conductivity of the electrolytic liquid is preferably 5 to 200 mS/cm.

[0109] In order to increase the polishing rate in electrolytic polishing and to prevent surface roughening of a polished surface, the electrolytic liquid preferably contains the same conductive material as a polishing object, e.g., copper, as a starting component. The concentration of such a starting conductive material, e.g., copper, in the electrolytic liquid is generally not less than 0.001% by weight, preferably not less than 0.005% by weight, more preferably not less than 0.01% by weight. The inclusion of a conductive material as a starting component in the electrolytic liquid can promote diffusion of the same conductive material, e.g., copper, or polishing products including the conductive material from a surface of a polishing object into the electrolytic liquid during polishing. The concentration of a starting conductive material, e.g., copper, in the electrolytic liquid is generally not more than 10% by weight, preferably not more than 1% by weight. This is because when the concentration of a starting conductive material is more than 1% by weight, the conductive material is likely to consume other component(s) of the electrolytic liquid. When the conductive material of a polishing object is a compound, the respective components of the conductive material may be contained in the electrolytic liquid as starting components in a proportion corresponding to the compositional ratio of the compound.

[0110] An example of the electrolytic liquid comprises (1) 2 to 80% by weight of an organic acid, (2) 2 to 20% by weight of a strong acid having a sulfonic acid group, (3) 0.01 to 1% by weight of a corrosion inhibitor, (4) 0.01 to 1% by weight of a water-soluble polymeric compound, (5) 0.01 to 2% by weight of abrasive particles, (6) 0.01 to 1% by weight of a surfactant, and an aqueous solvent. The aqueous solvent may be deionized water, preferably ultrapure water.

[0111] Electrolytic polishing using the electrolytic liquid of the present invention preferentially processes raised portions of irregularities present in a surface of a conductive material, such as copper, formed over a surface of a work-piece, such as a substrate, while protecting recessed portions of the irregularities with a corrosion inhibitor, thereby processing and flattening the surface of the conductive material. The electrolytic liquid is especially effective for use in electrochemical mechanical polishing which comprises electrolytically polishing a surface of a conductive material while rubbing the surface with a polishing pad. In particular, a protective film is first formed by a corrosion inhibitor on a surface a conductive material to prevent excessive etching, followed by rubbing of the surface of the conductive material with a polishing pad having appropriate hardness and flatness, thereby selectively removing the protective film formed on the surfaces of raised portions of the conductive material while leaving the protective film formed on the surfaces of recessed portions of the conduc-

tive material. By subsequent electrolytic polishing of the conductive material, the raised portions of the conductive material can be preferentially processed, whereby the surface irregularities of the conductive material can be smoothed out. A polishing pad for CMP, for example, can be used as the polishing pad.

[0112] A description will now be made of experiments on processing (polishing) of copper which were carried out with various electrolytic liquids, using a chip-testing machine capable of processing a 40 mm-diameter area. The chip-testing machine is capable of controlling the electrode potential of copper and performs processing of copper by polishing an exposed copper surface with a polishing pad attached to a processing table while applying a voltage between the copper and an opposing electrode. Polishing (processing) of copper was carried out by rotating the polishing table at 250 rpm (linear velocity 0.78 m/s at a position of 30 mm distance from the center) while pressing the polishing pad against a substrate sample having a copper surface at a pressure of 0.5 psi (35 g/cm²). During processing, current density or the electrode potential of copper was kept constant. Current density or the electrode potential can be measured even when the polishing pad is not in contact with a copper surface (pressure 0 psi) as in the below-described test for determining the effect of a corrosion inhibitor.

[0113] The substrate sample, which was used in the processing experiments, is a silicon substrate with a copper film (copper blanket wafer), having surface layers of: a oxide film (SiO₂) having a thickness of about 250 nm; a barrier metal film of TaN having a thickness of 30 nm; a copper seed film having a thickness of 100 nm; and a copper plated film having a thickness of 1500 nm, formed in this order.

A. Relationship of Various Organic Acids with Electrode Potential

[0114] Table 1 shows electrode potentials in polishing of the copper surface of the above-described sample wafer, carried out at a constant current density (40 mA/cm²) in an electrolytic liquid, using the above-described chip-testing machine and various types of organic acids in the electrolytic liquid. A lower electrode potential in the table indicates that a higher electric current will flow and thus the processing rate will be higher, as compared to a higher electrode potential, if processing is carried out to the same level of electrode potential. A lower electrode potential is therefore preferred.

TABLE 1

No.	Electrolyte	Concentration [mol/l]	pH	Electrode potential at 40 mA/cm ² [VvsAg/AgCl]
1	Malonic acid	1	4	4.03
2	Maleic acid	1	4	4.33
3	Citric acid	1	4	5.36
4	Glycolic acid	1	4	5.47
5	Malic acid	1	4	5.73
6	Glyoxylic acid	1	4	4.99
7	Ascorbic acid	1	4	7.55