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Optimization of the composition of the chemical copper plating solution in order to reduce the brittleness of the deposited copper coatings

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Abstract

The purpose of this work was to study ways to reduce the brittleness of copper layers during their deposition from solutions of thick-layer chemical copper plating. The introduction of various organic oxidants on the properties of the chemical copper plating solution, the rate of copper plating and the quality of the deposited copper layers from the tartrate solution of chemical copper plating has been tested. With the introduction of chloranil and anthraquinone, the rate of copper plating decreased. When benzoquinone, betanaphthoquinone, phenanthrenequinone, and xyloquinone were added to the chemical copper plating solution, the stability of the solution dropped sharply. The introduction of anthraquinone-2,6-disulfonic acid disodium salt (Na₂ADSA), nicotinic acid, pyridine and 2,2'-dipyridyl into the chemical copper plating solution had a positive effect on the properties of the obtained copper coatings with stable operation of the copper plating solution and a suitable rate of copper plating.

It is shown that a decrease in the plasticity of the copper coating is due to «hydrogen» brittleness, which is associated with the introduction of gaseous hydrogen into the copper coating during deposition, and «oxygen» brittleness, which can be caused by the inclusion of particles of monovalent copper in the coating in the form of copper oxide Cu₂O or copper hydroxide CuOH.

Desorption of hydrogen from the copper coating and, consequently, an increase in the ductility of the coating will be facilitated by an increase in the temperature of the chemical copper plating solution.

The introduction of additives to the solution of chemical copper plating, which reduce the rate of copper plating, will reduce the amount of hydrogen included in the chemically deposited coating.

It is possible to reduce the «hydrogen» brittleness of the coating by introducing organic oxidants into the solution of a tartrate solution of chemical copper plating. The

introduction of additives to the solution of chemical copper plating, which reduce the rate of copper plating, will decrease the amount of hydrogen included in the chemically deposited coating

It is shown that the accelerating effect on the process of chemical copper plating is exerted by the introduction of disodium salt of anthraquinone-2,6-disulfonic acid into the solution of chemical copper plating in an amount from $2 \cdot 10^{-6}$ to $6 \cdot 10^{-5}$ mol·l⁻¹. At the same time, there is an improvement in the plasticity of the deposited copper layer and an increase in tensile strength.

It was found that the addition of 2,2'-dipyridyl, in addition to affecting the «hydrogen» brittleness, also reduces the «oxygen» brittleness of the deposited copper layers. To obtain ductile copper coatings with a good deposition rate, the optimal concentration of 2,2'-dipyridyl was determined, which is 0.01 g·l⁻¹. Using this plasticizing additive, copper layers were obtained with a relative elongation of 4-5%, a tensile strength of more than 450 MPa, and a specific electrical resistance $(2.1-2.3) \cdot 10^{-8}$ Ohm·m. Optima were determined for the concentration of the additive, for the amount of air supplied to the copper plating solution, for the rate of copper plating.

Continuous bubbling of the chemical copper plating solution with air has been substantiated, and the optimal amount of supplied air has been established. The optimal bubbling rate is 0.26 l·min⁻¹ per 1 liter of chemical copper plating solution.

To avoid the possibility of copper passivation during deposition upon contact with atmospheric oxygen, deposition should be carried out in a chemical copper plating bath, divided by a partition into two zones, in one of which the solution is adjusted and bubbled with air, and in the other, copper coatings are deposited.

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