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Development of technological processes for surface preparation to electroless copper plating in the production of printed circuit boards

Abstract

Relevance of the research

The current pace of development of electronics and the tightening of requirements for the quality of finished products require an increase in the technical level of printed circuit boards (PCBs) – the basis of modern electronic devices and instruments.

Creating a strong electrical contact between the conductive pattern (CP) of the inner and outer layers of the PCB is a critical part of the PCB manufacturing process.

In practice, the most commonly used technology for this purpose is indirect metallization of holes using palladium activation of the dielectric surface, which is implemented in three stages. First, electroless copper plating is carried out – an autocatalytic reduction-oxidation process initiated by metallic palladium, a layer of which is formed on the dielectric surface at the preliminary activation stage. The metallic copper deposited on the activated dielectric surface subsequently acts as a catalyst for the process of electroless copper deposition. The thickness of the chemical copper layer is 0.3–1.0 μm. To strengthen the fragile layer of chemical copper, it is electrochemically covered with copper up to 7 μm thick, after which the conductive pattern is developed on the outer layers of the multilayer PCB – electrochemical build-up of copper up to 25–30 μm.

The quality of the electroless copper coating largely determines the properties of the entire metal layer and, ultimately, the reliability of the printed circuit board, which is why the requirements for it are becoming increasingly stringent. In turn, the quality of the electroless copper coating is largely determined by the preparation of the surface of the holes for its application. Surface preparation includes the stages of clean-conditioning, microetching and palladium activation.

Domestic standard technologies for the preparation of the surface of the holes of the PCB for electroless copper plating (GOST 23.770-79, OST 107.460092.028-96) date

back to the 70–90s of the last century and do not meet modern requirements for both technological characteristics (deposition rate of the chemical coating, service life and stability of solutions) and the properties of the coatings (adhesion strength to the base, continuity).

Later domestic developments also did not find practical application, since they are inferior to foreign analogues in the listed parameters and manufacturability. Domestic manufacturers of printed circuit boards are forced to either work with solutions prescribed by GOST and OST (defense industry enterprises), or use compositions of German, Swedish, Italian and other manufacturers.

The disadvantages of using imported products are their high cost and the need for a warehouse reserve due to the long logistics lead, as well as the risk of interruption of supplies in the context of sanctions.

In connection with the above, the development of domestic technologies for the preparation of surfaces of PCB holes for electroless copper plating, as well as the development of compositions for their implementation that meet modern requirements and are not inferior in characteristics to foreign analogues, is an important scientific and technical task, the solution of which is devoted to this dissertation.

The degree of development of the research. An analysis of scientific and technical literature, including patents, showed that there are no Russian developments of compositions for surface preparation before metallization of printed circuit board holes that meet modern requirements in terms of technological characteristics and coating properties.

The purpose of the work

Development of import-substituting technologies for clean-conditioning, microetching, palladium activation, allowing to obtain compact non-crumbling electroless copper coatings firmly bonded to the base deposited in the holes of the multilayer PCB not inferior to foreign analogues in terms of speed of covering the dielectric surface with a copper layer, as well as in the stability and resource of solutions.

The research tasks:

1. Study of the dependence of the functional characteristics of the colloidal

activator (rate of overgrowing the dielectric surface, stability) on the composition and temperature of the mixed activator components, the method and order of their mixing.

2. Study of the dependence of the functional characteristics of complex activators on the nature of ligands and the composition of solutions.

3. Study of the dependence of the ξ-potential of the dielectric on the composition of the conditioning solution.

4. Development of compositions for the preparation of the surface of printed circuit boards for metallization, as well as the development of a technological process for preparing the surface using the said compositions.

5. Conducting industrial tests of the developed compositions.

Scientific novelty of the research.

1. For the first time, the dependence of the hydrodynamic diameter (HDD) of the colloidal activator micelles on the composition, speed and order of mixing the solution components was established. It was shown that it is possible to achieve optimal values of the size of the palladium activator micelles and its maximum stability only with a two-stage mixing of the activator components, with the most stable colloidal systems forming at a Sn^{2+}:Pd^{2+} content ratio of 10:1 at the first mixing stage and 50:1 ratio in the resulting concentrate.

2. For the first time, it was established that the functional characteristics of the colloidal palladium activator depend on the size of the colloidal activator micelles:

– the rate of complete tightening of the activated surface of the PCB holes during electroless copper plating increases with a decrease in the predominant HDD of the activator micelles;

– the dependence of the stability of the colloidal activator solution on the HDD has an extreme character, the maximum stability of the solution corresponds to a predominant HDD of 105± 5nm.

3. For the first time, the fact of recharging the dielectric surface in the holes of the printed circuit board (from –17 to +44 mV in FR-4 and from –30 to +35 mV in polyimide) during conditioning in solutions containing hydrophilic cationic nitrogen-containing polymers K1 and K2 was experimentally established.

Practical significance of the research.

1. The theoretical significance of the work lies in establishing the patterns of influence of the parameters of the activator preparation process on the HDD of its micelles, as well as the influence of the HDD of micelles on the rate of metallization of the activated surface of the dielectric and the stability of the activator solution during operation and storage.

2. The practical value of the work lies in the development of a technology for the production of a colloidal activator concentrate by step-by-step mixing of intermediate compositions with ultrasonic treatment between the stages, which allows the formation of a colloidal system with an optimal predominant HDD of micelles and a narrow range of their dispersion, surpassing in operational characteristics the world analogues used in practice.

3. An anticoagulant was selected – a compound from the class of organic monoterpene aldehydes, which allowed an additional (2.5 times) increase in the stability of the colloidal palladium activator with an optimal micelle HDD (105 nm) in comparison with the currently used 4-hydroxy-3-methoxybenzaldehyde.

4. It has been shown that with an increase in the temperature of the mixed components of the colloidal activator concentrate to 60°C, the diameter of the formed activator micelles decreases, and a further increase in temperature does not affect the size of the micelles.

5. Nitrogen-containing surfactants (K1 and K2) have been established, the use of which in the clean-conditioning solution ensures the recharging of the dielectric surface before metallization, and it has been shown that this helps to reduce the time for the dielectric surface to be completely covered with an electroless copper layer.

6. Import-substituting technologies for clean-conditioning, microetching, palladium activation (colloidal and two complex activators) of the dielectric surface before electroless copper plating of through holes in printed circuit boards, as well as compositions for their implementation, have been developed that are not inferior to foreign analogues in terms of technology and achieved results.

Provisions for defense

1. Research results:

– dependencies of the functional characteristics of the colloidal activator (rate of overgrowing the dielectric surface, stability) on the composition and temperature of the component solutions, the method and order of their mixing;

– dependencies of the functional characteristics of complex activators on the nature of ligands and the composition of solutions;

– dependencies of the ξ-potential of dielectrics on the composition of conditioning solutions.

2. Technologies developed for preparing the surface of printed circuit boards before electroless copper plating and compositions for its implementation.

3. Results of testing the developed compositions in existing production.