Full Length Research Paper

Galvanic Deposition of Functional Plating in Non-stationary Electrolysis

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Abstract. The functional galvanic plating widely applied for electronic components, assembly by soldering or microwelding technology should possess a complex of the electro physical and mechanical properties providing high reliability of equipment. For formation of the set properties of plating the new methods of galvanic deposition in non-stationary electrolysis is perspective. Application of non-stationary electrolysis at deposit of silver and gold plating’s allows receiving at high efficiency of plating’s process with the fine-grained structure raised wear resistance and corrosion firmness at a small thickness, good a solderability and stably high durability of microwelded connections.

Keywords: Galvanic; Plating; Electrolysis; Non-stationary process.

1. INTRODUCTION

High-quality functional galvanic platings on the basis of precious metals - silver and gold have gained the high distribution in electronics. Electronics development reoriented technologies of galvanic deposition on reception of functional platings with high electro physical, technological and corrosion-prove properties. Along with the general requirements to galvanic platings, such as mechanical durability, non-porosity, firmness to atmospheric and to corrosive attacks, rigid demands are made to electro physical parameters: to specific and contact resistance, stability of these parameters under operating conditions, and also to the technological properties, providing weldability a solderability (Schlesinger et al., 2010).

One of the major and widely applied functional platings of electronic components are gilding. Gold differs high firmness to influence of excited environments, on electro-and heat conductivity concedes only to silver and copper. Gold forms low temperature connections eutectic type with Si, Ge and in which possess conductivity of certain type. Absence of oxide films and high plasticity of gold create conditions for reception of microconnections termocompression welding at temperature 300-320°C, and also soldering connections of a chip with the package.

The gold covering is applied in manufacture of printing and multilayered plates to maintenance of stable electric properties and a solderability of conductors, and also for contact surfaces of various design connectors that provides stability of contact electric resistance. Key parameters of a gold plating influencing quality of assembly operations are: hardness, cleanliness of a surface, electric conductivity, transitive electric resistance, porosity, a solderability. At a thickness of a gold plating to 3 microns it is necessary to provide hardness of coverings no more than 800 MPa, thus the gold maintenance in plating should be not below 99,99 %.

The resistance of electric contacts depends on many factors: specific electric conductivity, hardness, plasticity and corrosion firmness of platings, the area and a roughness of an actual surface of contact, conditions of plating deposition etc. Porosity of platings is most responsible for corrosion firmness of products. A pore in plating can settle down to perpendicularly substrate and under a corner to its surface, to have the different form, the sizes and character of distribution. In electronics gold use as a soft finishing plating for internal mounting of integrated curcits by a gold or aluminum wire, and also as firm - for electric connectors and contacts where low electric contact resistance is required. Recently soft gold plating was used for formation of matrix structure of conclusions of BGA package.

High cost of a gold plating, its deficiency and decrease in reliability of contact connections while in service cause of decrease in a thickness of a plating. Searches of ways of economy of precious metals have
led to working out of technology of deposition of thin gold coverings by thickness 0.1–0.25 μm. Decrease in a thickness of a gold covering about 3–6 μm to 0.1 μm demands maintenance of high quality of micro welded connections.

In manufacture of printed-circuit boards the plating from chemical nickel/gold immersion (ENIG) is applied, which represents thin (0.05–0.2 μm) the gold film put on an intermediate layer of nickel (4–5 μm). Gold is well dissolved in solder, is not subject to fast tarnishing and oxidation and provides the best planeness, than at HASL, at preservation good solderability (Cumbsa at al., 2008).

Equal, small crystal layer of gold provides well solderability and protects nickel from oxidation, and nickel carries out barrier function between copper and gold, preventing their mutual diffusion and the oxidation of copper conducting to formation of a surface not moistened with solder (Okinaka at al., 1998). Three kinds of defects of finishing covering ENIG are known also: plating porosity, fragile gold, and effect of “a black contact platform.

Essential lacks of silver platings is their low hardness and wear resistance, and also formation on a surface of sulphides and oxides. One of perspective directions of improvement of quality of functional platings is their deposition on a periodic current.

Application of periodic currents allows operating operatively technology of plating thickness formation, to lower quantity of included impurity and pores, to raise density and wear resistance of platings.

2. NON-STATIONARY ELECTROLYSES METHOD

The main features pulse electrolysis is: high instant density of a current which accelerate kinetics deposition and promote growth of kernels germs formation; presence of time of deenergizing of a current positively influences course of processes of ion adsorption and desorption, and also recrystallisation a deposit. Installations pulse electrolysis generates impulses of current amplitude from 10 to 200 A, duration of impulses from 50 to 100 ms and frequency of 10–1000 Hz. The form of current impulses is influenced by double electric layer on interphase border «electrode-solution». The double electric layer renders capacitor effect on duration and form of current impulses (Devaraj at al., 1990) (figure 1).

![Fig. 1: Influence of capacity of a double electric layer on the form of current impulses: initial impulses (a), an average (b) and strong influence (c).](image-url)

The total current develops of a current of deposition $J_F$ and capacitor current $J_c$:

$$J_t = J_c + J_F.$$  

(1)

The deposition current (component Faraday) is defined by following expression:

$$J_F = J_0 \left[ \exp \left( \frac{\alpha F \eta}{RT} \right) - \exp \left( \frac{1 - \alpha \eta}{RT} \right) \right],$$  

(2)

and a capacitor component - expression:

$$J_c = dQ / dt = Cd \eta / dt,$$  

(3)

where $a$ – a constant, $z$ –ion charge, $F$ – constant Faraday, $\eta$ – current exit, $R$– gas constant, $T$ – impulse duration, $C$ – capacity of double electric layer, $t$ – time.

New possibilities of formation of functional properties of galvanic plating give methods non-stationary electrolysis: alternation pulse, reverse and a dissymmetric alternating current. Non-stationary electrolysis installation is developed for formation of functional galvanic platings with programmed control electrolysis on the basis of the microcontroller (figure
2) in which automatically change: the current form, its amplitude, duration of impulses of direct and reverse currents, pauses between them, and also duration of work in various modes (Anufriev at al., 1988). Stabilization of an average and maximum current in loading about accuracy of 1 %, indication as breakage in a loading chain, and short circuit with automatic switching-off of installation is provided. The current measuring instrument defines the maximum loading both for direct, and for a reverse current with indication together with current values of parameters of the given cycle. Calculation and indication of quantity of the electricity which has passed through a galvanic bath that allows considering the metal expense automatically is provided.

Fig. 2: Scheme program-controlled installation of non-stationary electrolyses: MP – micro processor; ROM, RAM – memory; SINF – synchronization module; CM – current module; CDF – current direct former; IM – interfuse module; PSU – pulse supply unit; CC – computer control; CD – compact disk; FU – filter unit; GB – galvanic bath; A – anode; C – cathode.

Installation provides the maximum current of loading from 10 to 150 A, duration current impulse from 20 ms to 10 c, duration of a cycle of the program from 1 to 99 minutes. Non-stationary modes of reception of the high-quality platings are fulfilled, allowing raising their reliability and service life. At the initial stage deposition spend on a direct current in density 1,0–1,5 А/dm², then - on a pulse current in density 0,5–0,8 А/dm², frequency 10 Hz and on-off time ratio 3–5, and then - on reverse current in the ratio 4:1 (figure 3).

Fig. 3: The form of current impulses non-stationary electrolysis.

At pulse electrolysis coefficient of deposition cycle makes (Chadrasekar at al., 2008):

\[ K_D = \frac{T_{ON}}{T_{ON} + T_{OFF}} = T_{ON} f, \]  
(4)

and at pulse reverse electrolysis:

\[ K_R = \frac{T_C}{T_A + T_C}, \]  
(5)

where \( T_{ON} \) – duration of impulse, \( T_{OFF} \) – deenergizing time, \( T_A \) – duration of anode period, \( T_C \) – duration of cathodic period.

3. RESULTS AND DISCUSSIONS

At pulse electrolysis the current exit a for gold plating grows with 82 to 94 %, and porosity of thin plating (1,5–2,0 μm) decreases 400 to 10 pore/sm². Micro hardness silver platings from not cyanic baths with additives of ultradisperse diamond to 15 g/l, deposit pulse electrolysis, has increased with 0,7–1,0 to 1,4 GPa. If at long storage hardness of usual silver platings falls to 0,5 GPa, platings with ultradisperse diamond - to 0,9 GPa. This results from the fact that
Khmyl and Lanin

Galvanic Deposition of Functional Plating in Non-stationary Electrolysis

There is a crushing of a deposit and reduction of the size of blocks of a mosaic about 30,0–31,1 nanometers to 29,5 nanometers as the adsorbed microparticles of diamond interfere with growth of grains. As a result of crushing of structure, more dense packing of crystals and increases in a basic surface of layers for the account of smoothing of their relief 2–4 times wear resistance of silver platings raise.

The parameter of a lattice of platings with inclusion of diamond microparticles f increases with 4,0785 to 4,0863 A, that is caused by increase in the maintenance of impurity in a deposit. In silver deposits the axial structure with an axis [111] which practically does not change with growth of concentration of diamond microparticles in electrolyte is realised. Change of parameter of a lattice causes change of a sign on internal pressure in platings.

For silver platings with microparticles of diamond pressure of the compression which size makes 0,25–0,27 GPa at 1 A/dm$^2$ and 0,16 GPa at 3 A/dm$^2$ are characteristic. To increase in the maintenance of microparticles in electrolyte there is a growth of internal pressure. The current exit of silver platings in a working interval of density of a direct current is close to 100 %, and on a pulse current on frequency of 10 Hz and average density of a current 1 A/dm$^2$ – 96–99 % and depend on on-off time ratio a little.

Contact resistance of silver platings and platings silver - diamond at loading 100 g are close and make 1,4–1,7 mΩ, that speaks pseudo-alloy formation as the second phase does not react with a matrix. Estimation of a solderability of silver platings on spending factor the dosed out preparation of Sn-Pb solder in weight of 250 mg at presence rosin flux at temperature 220±5°C are resulted in Table 1. Solderability deterioration is observed only at increase in concentration of microparticles of diamond at 15 g/l in electrolyte. On value of factor spreading 80 % a solderability of composite silver platings there are more it is possible to consider good (Lanin at al., 2000).

Table 1: Solderability silver platings

<table>
<thead>
<tr>
<th>Diamond maintenance, g/l</th>
<th>Spreading coefficient, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>J = 1 A/dm$^2$</td>
</tr>
<tr>
<td>0</td>
<td>82,7</td>
</tr>
<tr>
<td>5</td>
<td>82,2</td>
</tr>
<tr>
<td>10</td>
<td>79,6</td>
</tr>
<tr>
<td>15</td>
<td>77,5</td>
</tr>
</tbody>
</table>

Corrosion firmness of platings is defined by registration of polarizing curves and calculation of speed of a current of dissolution at anode polarization. Currents of dissolution of a usual silver plating in the thickness 6 μm, received at 1 A/dm$^2$ have made 0,14 μA/mV, and at 0,3 A/dm$^2$ - 0,05 μA/mV. Lower density of a current allows forming more corrosion proof platings. Introduction of a micropowders of diamond with concentration 15 g/l in electrolyte, has allowed to receive a plating with a current of dissolution 0,15 μA/mV, and application of a non-stationary mode electrolysis has lowered a current of dissolution to 0,04 μA/mV.

With increase in on-off time ratio of a current corrosion firmness of platings increases. It is caused by reduction of the size of grains and increase of density of layers, overlapping of a through pore for the account of interruption of process of sedimentation and formation of multilayered plating. The analysis of morphology of a surface, deposited on various modes electrolysis, on REM «Hitachi» S-806 is resulted in Table 2.

Table 2: Surface morphology of platings for various modes electrolysis

<table>
<thead>
<tr>
<th>Deposition mode</th>
<th>The average size of grains, μm</th>
<th>Quantity of grains on area unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>DC 1 A/dm$^2$</td>
<td>0.6 – 0.8</td>
<td>30</td>
</tr>
<tr>
<td>PC q=1,25</td>
<td>0,3–0,4</td>
<td>40</td>
</tr>
<tr>
<td>PC q=2</td>
<td>1.6 – 2.5</td>
<td>6</td>
</tr>
<tr>
<td>PC q=3,5</td>
<td>1,2 – 1,8</td>
<td>5</td>
</tr>
<tr>
<td>RC f=4,5</td>
<td>0,8 – 1,2</td>
<td>9</td>
</tr>
<tr>
<td>DC+PC</td>
<td>0,6 – 1,1</td>
<td>11</td>
</tr>
<tr>
<td>DC+RC</td>
<td>1,2 – 2,3</td>
<td>3</td>
</tr>
<tr>
<td>DC+PC+RC q=2</td>
<td>0,4 – 1,2</td>
<td>8</td>
</tr>
<tr>
<td>DC+PC+RC q=3,5</td>
<td>0,5 – 1,5</td>
<td>6</td>
</tr>
</tbody>
</table>

The plating’s deposited by a pulse current at low on-off time ratio q=1,25, have fine-grained structure. With increase in porosity the structure becomes more granular, but thus and more plastic. Surface morphology of platings for various modes electrolysis is shown on figure 4. Application of non-stationary modes electrolyses promotes considerable improvement of wear resistance and corrosion firmness that provides decrease in a thickness of a plating and economy of precious metals.
Electrolysis programmed modes influence on microwelded joint strength. Pulse current causes coating structure refining as the certain crystallite growth is limited by current pulse duration. It is also experimentally found that under these conditions the quantity of organic-like impurities incorporated into coating decreases. High pulse current density favours minimizing substrate effect on the film crystalline roughness of thickness up to 0.5–1.0 μm. This factors leads to increase of microwelded joint strength to direct pull from 8.6 to 12.3 sN for gold layers and from 11 to 14.3 sN for Ni ones.

At reverse current deposition during dissolving the plating hydrogen is deposited simultaneously with the metal structure. The surface roughness and internal stresses in films decrease. Under these conditions microwelding strength to direct pull increases and the number of defect joints and contact transient resistance decreases.

Successive alternation of the electrolysis modes according to specific program which provides metal plating at DC, PC and RC results in the plating formation of individual density packed monolayers of 0.01–0.05 μm in thickness. Practically each layer like this completely suppresses the possibility to continue normal growth of underlying crystals. The plating structure being formed and crystalline roughness are solely determined by the electrolysis conditions. This result to more smoothed micrelief surface of plating and it there appears easiness of ultrasonic microwelding realization and joints high quality. Durability of the microwelded connections received on platings, deposited on a pulse current, depends on a current on-off time ratio. With increase in on-off time ratio to 3.5 durability of microwelded connections raises to value 16.7 sH. The further increase in on-off time ratio conducts to reduction of durability of microwelded connection because of reduction of wire contact area with plating and increases in the surface roughness. Non-stationary modes electrolysis makes considerable impact on structure and property of gold coverings: reduction of parameter of a lattice, the sizes of blocks, internal pressure, etc. In the platings formed on periodic currents the size of blocks of a mosaic decreases to 242°A, pressure of a stretching pass in pressure of compression. The most perfect structure of platings is received on frequency of 25 Hz and on-off time ratio 2.

4. CONCLUSION

Application of non-stationary modes electrolysis at deposit of silver and gold platings allows receiving at high efficiency of process electrolysis platings with the fine-grained structure raised wear resistance and corrosion firmness at a small thickness, good a solderability and stably high durability of microwelded connections. Introduction of microparticles of diamond raises wear resistance of composite silver coverings in 2–4 times, crushes structure provides more dense packing of crystals and increase in a basic surface of layers at the expense of smoothing of their relief. Use of such platings at manufacturing of modern products of electronics allows applying local silvering and gilding with smaller thickness without deterioration of their quality that provides economy of precious metals and reduces the cost price of manufacturing of products.

REFERENCES


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