SILVER COATINGS PLATED BY ELECTROLESS METHOD

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Keywords: *Silver coating, immersion plating, solderability, corrosion resistance.*

Abstract: *The immersion silver plating is on the focus of the present work. The ecological technology is established on the base of the developed stable solution, avoiding the use of cyanide ions. The obtained coatings are uniform, dense with good solder wettability and high corrosion resistance suitable for application in a production of printed circuit boards.*

СРЕБЪРНИ ПОКРИТИЯ, ОТЛОЖЕНИ ПО БЕЗТОКОВ МЕТОД

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Ключови думи*: Сребърни покрития, имерсионен метод, спойваемост, корозионна устойчивост.*

Резюме: *Имерсионният метод за отлагане на сребърни поктития е във фокуса на представеното изследване. Утвърдена е екологична технология за нанасяне на сребърни покрития, основаваща се на разработен стабилен разтвор без използване на цианидни йони. Получените покрития са плътни, равномерни с добра спойваемост и висока корозионна устойчивост, подходящи за приложение в производството на печатни платки.*

Introduction

Immersion plating is a simple and low cost process for production of uniform, dense and adhering layers of nobler metals to less noble metal. The process runs without an external source of current in an aquatic environment due to differences in the levels of oxidation potentials of the metal ions being deposited and the metal ions being displaced. The reaction continues until the coating completely covers the plated surface. Therefore the result is in obtaining of a thin layer [1].

Immersion plating by different metals such as silver, tin, electroless nickel/immersion gold (ENIG) are used as a surface finishes for protection the copper metallization of the PCB from oxidation enabling good solderability during the period of storage. The advantages of these processes are the transition to lead-free electronics.

Immersion silver (ImAg) has emerged as an alternative finish for lead-free assemblies. The silver layer serves as a protective finish, thereby ensuring the solderability and a corrosion protection of the underlying copper, also easy assembly and low cost. ImAg has good wettability and solderability compared to various lead-free finishes—not as well as ENIG, but better than immersion tin (ImSn) and organic solderability preservatives (OSP). During the assembly process the ImAg finish coating is dissolved into the molten solder because of liquidation of silver into the tin (Sn) based in the solder reaching the underlying base copper surface and obtaining a good wettability [2, 4, 10].

Conventional methods for silver plating both by electrodeposition and via immersion plating use hazardous cyanide compounds as a complex agent. New studies, however, aim at replacing the cyanide anions with other complexing agents (Table 1) for obtaining environmental friendly plating solutions [3, 11, 12].

The thickness of ImAg layer is typically less than 1 μm. It is happen because the deposition of Ag process will be stopped when the substrate surface is fully covered with the Ag solution [5]. Some researchers report that the thickness of immersion silver must be not too thick due to brittle solder joint in lead-free soldering, and not too thin to ensure a lifespan of this surface finish during storage [6 - 8].

ENIG has been the primary, high performance surface finish used in the PCB industry for some decades now. Mac Dermid has developed a high performing and economically viable alternative as electroless nickel/immersion silver (ENImAg) process that eliminates the concern associated with the use of a high priced metal, such as gold and its aggressive nature of the chemistry [9].

Another method for silver plating running without external current is electroless plating method. It is a preferred method for uniform deposition of metals on too complicated surfaces ensuring thicker coatings. Electroless plating involves the deposition of a metallic coating from an aqueous bath onto a substrate by a controlled chemical reduction reaction which is catalyzed by the metal or alloy being deposited or reduced.

Despite the advantages of Silver as a plating metal due to its high electrical conductivity, corrosion resistance and good friction and wear properties, there are too many problems caused by the present coating techniques. They are very expensive and use aqueous plating baths containing extremely toxic cyanide compounds and other compounds that contaminate the silver plating [13, 14, and 15].

Elaboration of new inventions by using of novel reducing agent which consists of thiosulfate and sulfite shows a plating rate and plating solution stability far superior those of conventional silver plating solutions moreover avoiding ammonia or cyanide ions as a plating constituent [16].

Rather perfect internal structure of silver coatings is obtained using Co (II) as a reducing agent. Presumably this leads to adsorption of cobalt compounds inhibiting the free growth of silver crystals [17].

The aim of the present study is to develop an ecofriendly simple technology for silver plating, ensuring to obtain dense, corrosion resistance, well solderable coatings suitable for application in a production of printed circuit boards using a stable silver plating bath.

Experimental and test methods

Copper, brass and electrolessly coated by nickel steel samples are used as a substrate material for electroless silver plating. Specimens are degreased ultrasonically in acetone. The following pre-treatments for electroless plating include both degreasing and microetching in acid solution composition 100 ml/l H_2SO_4 and nonionic surfactant 0,1 g/l (for copper and brass samples) and degreasing and microetching in acid solution composition 50 weight % HCL(for nickelized details) at room temperature for 2-3 min., carefully washing with distilled water.

Electroless baths for sиlver plating are known to be difficult to stabilize as during the plating process the silver reduction in the solution volume is observed. Also these solutions are characterized by a low deposition rates. So developing a stable and productive solution is a top priority. Conventional baths consist of hazardous cyanide ions as a complex agent typical for solutions with reduction agent BH_4^-. Development of ecofriendly solution avoiding cyanide ions demands selection of new reducing agents with proper complex agents maintaining a sufficiently low concentration of silver ions, which ensures its uniform deposition. The following complex agents are studied ammoniacal, ethylenediamine, rhodanide, fluoride. The choice is in favor of ammonia complex in terms of availability and price. The suitable reducing agents for ammoniacal solutions are invert sugar, glucose, hydrazine, potassium sodium tartrate, formalin, some metal ion, EDTA. More detailed research work are performed with invert sugar and some metal ions such as Cu(I), Fe(II and Co(II). The composition of used silver plating bath is listed in Table 1.

Table 1. Composition of silver plating bath

Bath constituents and parameters	Quantity	Bath constituents and parameters	Quantity
Silver salt	0.01 0,3 M		
Complex agent (NH_4OH)	0,66 – 10 M	Rate S/V	1,5-3,0 dm^2/l
Stabilizer	0,5 – 2 M	Temperature	20° - 40°C
Reducing agent	0,01 – 2 M	Time of etching	Depends on the desire thickness

Thickness of the coatings is measured by UPA Technology X-Ray Instrument. Features include laser focusing, point and measure, easy-to-load sample stages, and plating bath analysis using Low-energy soft X-Rays, based on a change to X-Rays transmitted. The gage's software is designed to be user-friendly with drop-down menus and a Microsoft-based operating system that enables direct transfer of measurement date to Excel.

For solderability investigation of silver layers the solder spread test is used by the contact angle measurement. The lead free solder wire is used. The solder of 0,036-0,038 g is heated at 250 °C to the melting of the wire [16].

The silver coatings characteristics are investigated after deposition and after aging (corrosion test) for 10 days in an Air Humidity Chamber above the following condition: 93±3% relative humidity and T=40±2 °C, which represents storage over few months.

Results and discussion

The plating solution with first two reducing agents containing Cu(I) or Fe (II) ions gives a slow deposition rate and reduction reaction in the volume. The dependence of the coating thickness on the deposition time using different reducing agent is presented in Figure 1 and Table 2.

Table 2. Dependence of the coating thickness on the deposition time using different reducing agents

Deposition time (τ, min)	Coating thickness, µm				
	Cu(I)	Fe(II)	Co(II)	Invert sugar	
	40°C	40°C	40°C	40°C	60°C
10	0,5	0,5	1,0	1,2	1,5
20	1,0	1,5	1,5	2,0	2,8
30	Volume reduction	Reaction stops	2,5	3,2	4,0
60		-	4,0	4,0	6,0

The plating solutions with Co (II) and invert sugar reducing agents work with increased stability up to plating of surface area of 10 m^2.

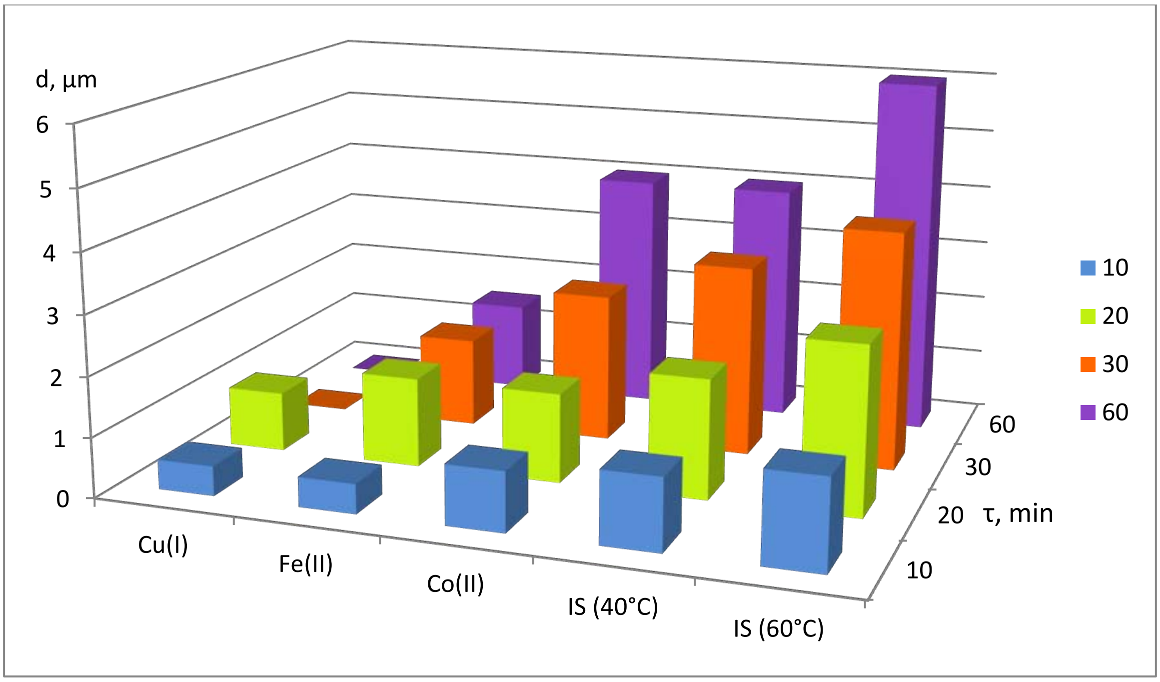

Fig. 1. Dependence of the coatings thickness (d) on the deposition time (τ)

Co(II) plays a role of a reducing agent of silver ions only in a presence of ammoniacal compex agent. The formation of more sustainable complex with Co(III) in an ammoniacal solution facilitates oxidation process of Co(II) ions and reduction of Ag(I) ions to Ag atoms. The deposition rate is proportional to the working temperature, but on the other hand the increasing of the working temperature leads to a volume reduction of Ag(I). The reduction of the Ag(I) in the volume is observed after 40 °C for reducing agent Co(II) and after 60 °C for reducing agent invert sugar.

The solderability measurements are carried out in case of using Co(II) as reducing agent to 40 °C and for invert sugar to 40 °C and to 60 °C for a time period of 0-60 minutes. The results are shown in Figure 2.

It is observed that the solderability of the coatings decreases with the deposition time for all of the tested coatings. The presence of divalent ions of Co(II) in plating bath at 40 °C shows better result for solderabilitry than this one for the coatings obtained at 60°C with reducing agent invert sugar after an hour. But the solution with Co(II) is unstable at higher temperature. The using of invert sugar as a reducing agent shows better soldering characteristics of the obtained coatings at 60 °C than this one of the cotings with Co (II) to 40 minutes of plating time. The best results are achieved for the coatings produced with reducing agent invert sugar at 40 °C, i.e. the contact angle has the lowest value for the entire deposition interval.

No corrosion evidence is observed after aging of the coatings obtained with Co (II) and invert sugar reducing agents at 40 °C plating temperature in an Air Humidity Chamber at above mentioned conditions. Good corrosion resistance is due to uniform, equal silver layers with grains characterized of fine structure. The test performed for solderability measurement of all of the examined coatings shows no influence of the corrosion aggressive environment on the contact angle.

The developed solutions for electroless silver plating remain stable within the research period of one year.

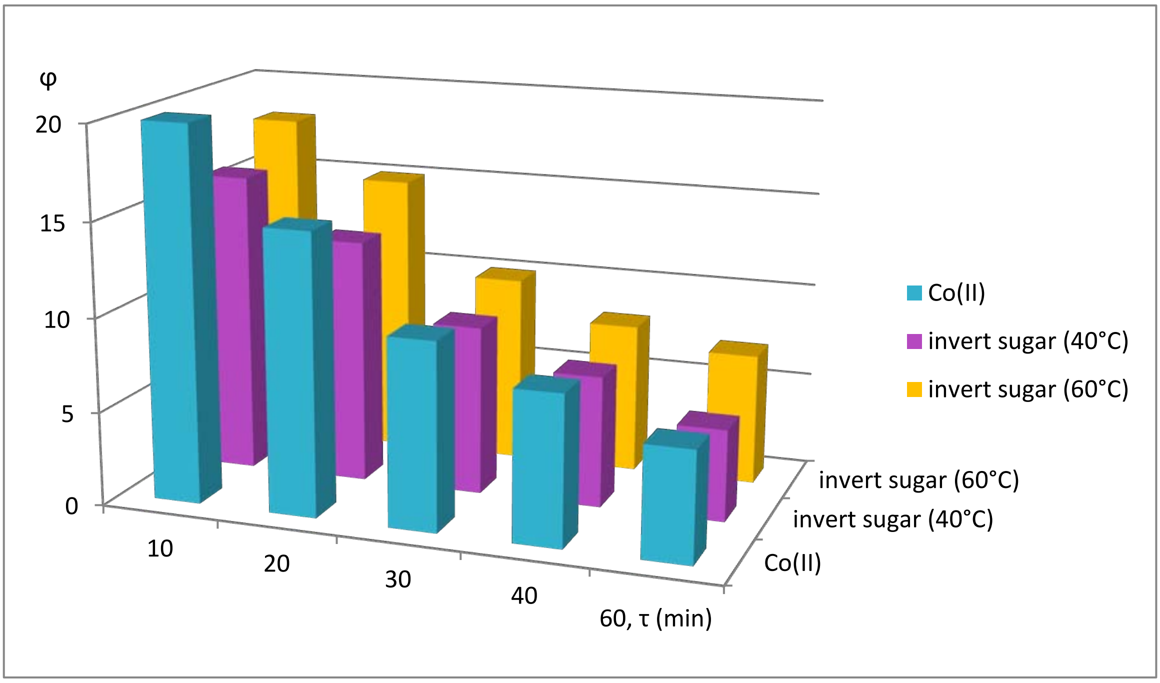

Fig. 2. Dependence of the solderability on the deposition temperature

Conclusions

A novel solution for electroless silver plating is developed on the base of ammoniacal complex formation and reducing agents Co (II) or invert sugar.

The innovation is in the establishment of a stable plating bath more than a Year, avoiding hazardous cyanide ions, also allowing obtaining more than 10 dm^2 coated surface.

The established technology mode ensures obtaining uniform, equal silver coatings with fine structure, ensuring best corrosion resistance after aging and good solderability both after deposition and after aging

The increase of the silver deposition rate at higher working temperature is determined. Decomposition of the plating solution is found out at 40 °C when reducing agent of Co (II) is used and after 60 °C for reducing agent of invert sugar.

The thickest coatings are obtained with reducing agent of invert sugar at 60 °C working temperature.

Addition of reducing agent of Cu (I) leads to solution decomposition after achievement coating thickness of 1 µm, while using Fe (II) as a reducing agent the reducing reaction stops after 20 minutes from the beginning of the process.

Measurement of the coatings solderability shows the deterioration of the received results with the working temperature increase in case of using the invert sugar as reducing agent.

Comparison of the received solderability data for all of the tested coatings gives the best result for coatings obtained with reducing agent of invert sugar at 40°C working temperature.

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