Electrodeposition of functional silver coatings from buffered baths

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In this work, conditions for the deposition of functional silver coatings from dicyanoargentale-borate-phosphate-carbonate bath on silver, platinum and materials that are widely used to manufacture integrated-circuit packages (nickel, kovar, copper and copper-tin alloys) are described. Methods for the surface preparation of various materials before silver plating were employed; they made it possible to ensure a firm adhesion of the coating to the base material without using poisonous, professionally harmful operations such as copper and silver plating from cyanide electrolytes, amalgamation.

Electrolyte composition and electrolysis conditions are proposed for depositing functional silver coatings without gold sublayer. Its optimal composition is (g/l): $KAg(CN)_2$ 30–45; K_2CO_3 5–6; K_2HPO_4 8–12; KH_2PO_4 10–15; H_3BO_3 20–25; pH 7 ± 0.1, at a temperature of 55 °C. It has been shown that by varying electrolysis parameters, coatings with desired functional properties meeting the needs of microelectronics industry can be formed.

Key words: silver, electrodeposition, coatings, adhesion, surface treatment

INTRODUCTION

Electronic industry and production of microelectronic devices competitive in the world market demand quality and cheap functional silver coatings, which are on a par with gold coatings, call for the reduction of the consumption of resources and require developing highly efficient and economical silver plating technologies. Regardless of the rare attempts to apply baths not containing cyanides for silver electroplating [1–4], currently galvanic silver deposits for practical purposes are deposited mainly from solutions containing $Ag(CN)_x^{1-x}$ complexes as a source of silver and some amount of free cyanide ions or buffer additives (*e.g.*, [5–14]). Such baths in the presence of various additives are widely used for functional silver coating electrodeposition (especially instead of gold coatings) for the fabrication of electronic devices. However, these electrolytes are extremely toxic and do not allow silver coatings to be applied to a substrate of copper, brass and nickel alloys without intermediate layer deposition. At the present time, an intensive search is under way for new electrolytes, which would make it possible to solve problems of depositing adherent coatings with tailor-made technical characteristics (transition re-

sistance, microhardness, solderability, etc.). The main ways of improving the silver plating processes are the development of new modern electrolytes and optimization of the deposition conditions. For these purposes, dicyanoargentate-borate-phosphate-carbonate (BPC) bath might be considered. The environmentally friendly and usable BPC baths for silver plating have a number of advantages against cyanide baths. They are less toxic as they have no excess cyanide ions and make it possible at the same time to deposit sound adherent coatings with lasting bath operation [5, 6].

Silver plating on electronegative metals is a complicated problem, since the firm adhesion of electrodeposited silver to the substrate material is not achieved due to the contact deposition of silver. The reasons for the formation of silver layers, loosely bound to the surface, on reactive metals in silver plating electrolytes are considered in [9]. It has been shown that it is possible to avoid this effect and to improve the adhesion of silver electrodeposits by surface preparation or adding some organic admixtures to the electrolyte. A firm adhesion between the base metal and the silver coating is achieved either by amalgamation or by the pre-deposition of a pretty thin silver film from electrolytes with a low silver

ion concentration and a high cyanide concentration [10, 11]. Copper and its alloys containing no large amounts of nickel are successfully subjected to amalgamation. The following solutions are recommended for amalgamation (g/l): 1) $HgCl_2$, 7.5; NH_4Cl, 4.2; 2) HgO, 7.5; NaCl, 60; 3) $K_2Hg(CN)_4$, 5–10; KCN, 10–20. Moreover, some special cases of silver electroplating on various substrates and surface pretreatment procedure are reported in [12]. For instance, in order to achieve good adhesion between electrolytic silver coating and copper substrate it is proposed to treat the copper surface for 1–1.5 min in chromic acid and then to degrease it by washing in the 5–15% sulfuric acid solution. During this procedure a passive film is formed on the surface, which prevents the contact silver deposition but does not hinder the electrodeposition of silver. When silver is electroplated on iron, nickel and iron–nickel alloys, it is necessary to deposit a thin film of silver from a silver pre-plating bath with a high cyanide concentration. To deposit such a layer of silver, electrolytes of the following composition and the following process conditions are recommended: AgCN, 3.7–5.2; KCN, 75–90; temperature, 20–30 °C; $j_C = 1.6$–1.7A dm^{-2}. The devices are immersed with the current on, and in all cases a high initial current density, which is 2.5 times higher than the working value, is recommended in order to suppress contact exchange.

The employment of these methods for the surface preparation of various materials prior to silver plating ensures a firm adhesion of the coating to the base material, but requires the use of poisonous professionally harmful substances and operations (copper and silver plating from cyanide electrolytes, amalgamation). Therefore, the main goal in the development of silver plating technology is development of the technologies and electrolytes that make the use of toxic substances unnecessary.
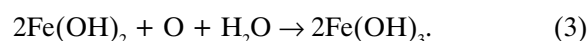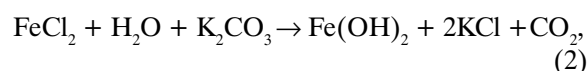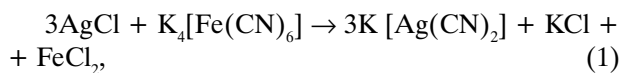
The objective of this work was to optimize the composition of a relatively environmentally friendly dicyanoargentate-borate-phosphate-carbonate buffered bath with respect to the main constituents that enable to deposit silver with required mechanical properties and surface morphology in order to fit the needs of microelectronics industry.

EXPERIMENTAL

Working solutions were prepared from chemically and analytically pure preliminarily recrystallized reagents. The pH was kept at 7.0 ± 0.1 and corrected by adding boric acid.

The electrolyte was prepared by two methods. When the electrolyte was formulated by the method described in [10, 13], the following ingredients

were used: as-precipitated silver chloride, potassium ferrocyanide and potassium carbonate. The amount of the last two ingredients was three times larger than that of silver chloride. Potassium hydroxide and potassium ferrocyanide were dissolved separately and heated to boiling. After short boiling, both solutions were poured into a vessel with silver chloride and boiled, keeping light out, for 1.5–2 h. The following reactions tooke place during the boiling:

$$3AgCl + K_4[Fe(CN)_6] \rightarrow 3K\,[Ag(CN)_2] + KCl + FeCl_2, \tag{1}$$

$$FeCl_2 + H_2O + K_2CO_3 \rightarrow Fe(OH)_2 + 2KCl + CO_2, \tag{2}$$

$$2Fe(OH)_2 + O + H_2O \rightarrow 2Fe(OH)_3. \tag{3}$$

The greenish-brown iron(II) hydroxide formed was changed into $Fe(OH)_3$ by means of hydrogen peroxide, precipitated and filtered off. The filtered off electrolyte was light yellow in color. The solution obtained was analyzed for silver(I) and iron (II) content.

Besides, the solution was prepared directly from potassium dicyanoargentate for comparison with the electrolyte under investigation. A weighed amount of $KAg(CN)_2$ was dissolved in twice-distilled water.

A BPC buffer was added to solutions obtained by different methods; it increased the ionic strength of the solution and stabilized the state of the ions in the bulk electrolyte and in the cathode layers during electrolysis.

Functional silver coatings were deposited on copper, Cu–Sn (0.15%) alloy, nickel and kovar specimens with the working areas 2 cm^2.

Before applying silver electrodeposition, regardless of the substrate metal, all specimens were degreased by an electrochemical method in an electrolyte containing NaOH, Na_2CO_3 and Na_3PO_4 (25 g/l each) and a wetting agent OC-20 (0.05 g/l). Degreasing was performed at a current density of 5A dm^{-2} at 55 °C for 5 min. on the cathode and 1 min on the anode. The auxiliary electrode was a sheet of nickel foil.

Then the copper electrodes and Cu–Sn alloy electrodes were treated in a bright pickling solution consisting of acids (orthophosphoric acid 940 g/l, nitric acid 280 g/l) with the addition of 0.25 g/l thiourea at room temperature for 1 min, rinsed and activated for 2 min in a hydrochloric acid solution (1:1 by volume).

After degreasing, the kovar specimens were treated for 2 min in a sodium bisulfate solution (60 g/l) in the presence of OC-20 (0.05 mg/l) at room temperature, rinsed and kept for 30 min in a 0.05% sodium sulfate solution.

After degreasing, the nickel specimens were pickled for 2 min in a hydrochloric acid solution (2:1), washed and kept in a 20% citric acid solution for 30 min.

Then, a 6–8 μm thick silver coating was deposited on the specimens prepared in this way, at 55 ± ± 0.1 °C. The temperature of the solutions was maintained with the aid of a thermostat UTU-4.

The quality of the coatings deposited was assessed visually and with a LEO-435VP scanning electron microscope (Germany).

The adhesion strength and porosity of the silver coatings deposited on the substrates under study were checked according to GOST 9-302-88.

After deposition the specimens were degreased with ethanol, washed with distilled water and dried with filter paper. The measurements were carried out at room temperature.

The adhesion strength was determined by the mark technique.

The porosity of coatings was determined by applying filter paper damped in a solution (g/l): $K_3[Fe(CN)_6]$, 3; NaCl, 10.

Microhardness was measured on a PMT device by the indentation of a square-base diamond pyramid with an apex angle of 136° between the opposite faces under a load of p = 50 g.

RESULTS AND DISCUSSION

A 6–8 μm thick silver coating was deposited on prepared specimens at different current densities from dicyanoargentate-borate-phosphate-carbonate (BPC) baths with a silver concentration of 0.13 mol/l, which had been prepared by different methods: the first electrolyte (I), proposed by us, based on AgCl and potassium ferrocyanide and the second electrolyte (II) based on $K[Ag(CN)_2]$.

The coating of silver and platinum specimens were in all cases of silvery-white color, fine-crystalline, without metal penetrations and spots in a current density range of 0.5–1.5 A dm^{-2}.

The coatings on copper and Cu–Sn alloy substrates were dense, uniformly distributed over the surface and homogeneous in structure.

Figure 1 shows scanning electron microscopy (SEM) images of silver coatings deposited on a copper-tin alloy substrate at different current densities in solution II. One can see that the silver deposit obtained at low current densities (0.5 A dm^{-2}) has a homogeneous close-packed fine-crystalline structure.

The coating structure becomes coarser-crystalline with increasing current density. For instance, at a current density of 0.75 A dm^{-2} (Fig. 1, b), isolated crystals of practically the same size are obser-
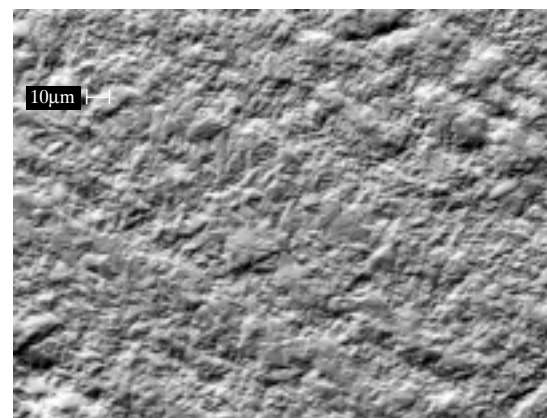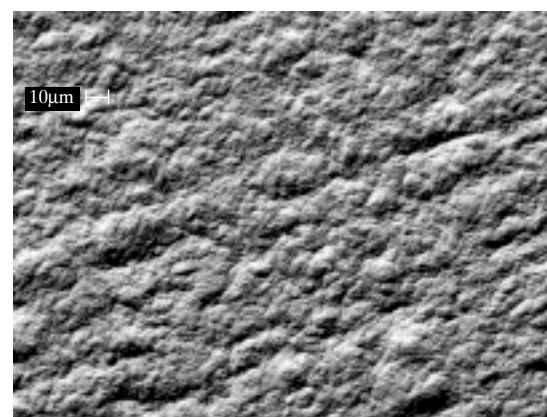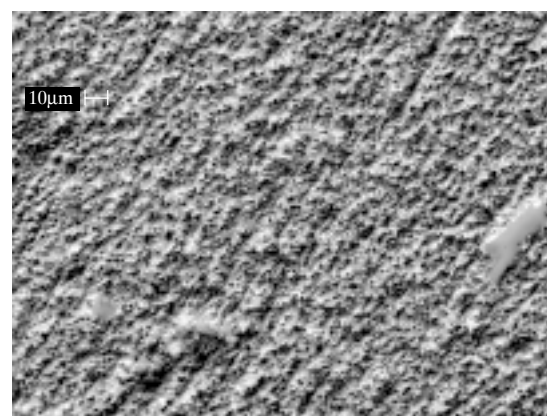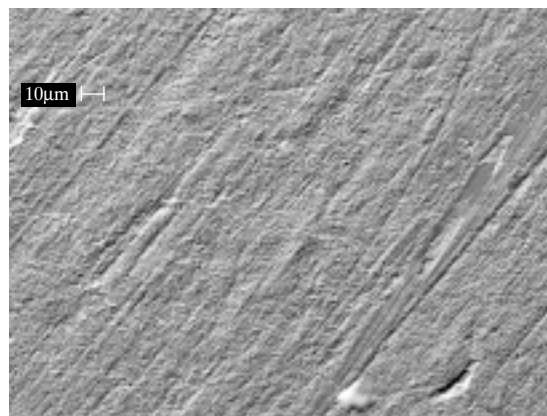

Fig. 1. SEM images of silver coatings deposited on Cu–Sn alloys (0.15%) at different current densities (A dm^{-2}) : (*a*) 0.5, (*b*) 0.75, (*c*) 1.0, (*d*) 1.25
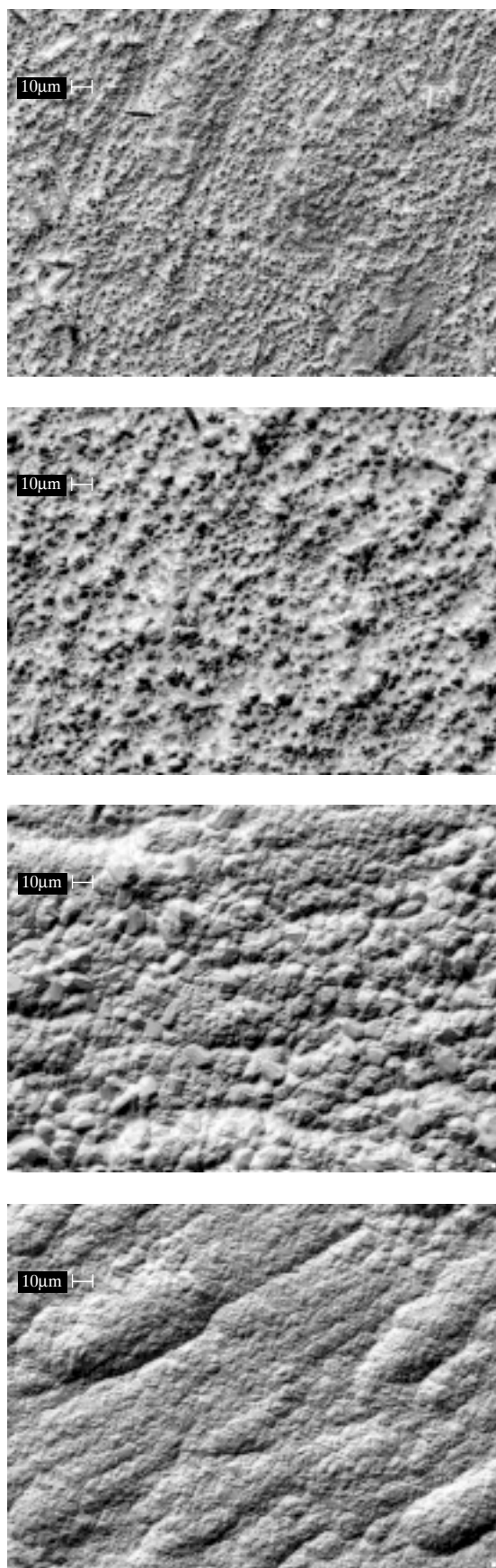
Fig. 2. SEM images of silver coatings deposited on nickel at different current densities (A dm^{-2}) : (*a*) 0.5, (*b*) 0.75, (*c*) 1.0, (*d*) 1.25

ved on the silver surface. As the current density increases to 1.0 A dm^{-2} (Fig. 1, c), the coating structure becomes close-packed, but the crystal size is larger than at low current densities. When the current density is further increased to 1.25 A dm^{-2} (Fig. 1, d), the coating structure becomes coarse-crystalline, and the size of some crystals reaches several square micrometers.

A similar picture was observed when silver coatings were deposited from the same electrolytes on a nickel substrate, but at high current densities (Fig. 2, c and d).

At low current densities (0.5 and 0.75 A dm^{-2}), the coatings were loose and inhomogeneous (see Fig. 2, a and b), and individual crystals or groups of crystals were observed on the surface, which may be due to hindered silver crystal nucleation.

An inhomogeneous loose structure and a non-uniform distribution were observed in coatings on a kovar substrate. In this case, it is apparently necessary to update the technology for surface preparation prior to silver deposition.

Sound deposits (visually) and a high current efficiency (97–98%) on copper and nickel substrates were obtained at a current density of 0.75–1.25 A dm^{-2} in the both electrolytes investigated. On kovar at a current density of 1.5–1.7 A dm^{-2}, the coating was somewhat better in electrolyte I than in electrolyte II.

The results of the current efficiency for silver electrodeposition as a function of current density in the baths are presented in Tables 1 and 2.

As is seen from Table 1, the use of electrolyte I makes it possible to obtain sound coatings on copper and nickel with a high current efficiency (92–96%) in the whole range of the current densities studied. The low current efficiency at low current

Table 1. **Current efficiency (%) for silver as a function of current density in Bath I**

Substrates	Current density, A · dm^{-2}				
	0.5	1.0	1.25	1.5	2.0
Copper	92.4	98.4	97.5	96.9	96.1
Nickel	99.1	97.8	96.8	95.8	90.7
Kovar	70.9	72.7	71.6	80.0	87.9

Table 2. **Current efficiency (%) for silver as a function of current density in Bath II**

Substrates	Current density, A · dm^{-2}				
	0.5	0.75	1.0	1.25	1.5
Copper	92.4	95.5	79.3	74.5	67.1
Nickel	89.4	91.0	87.2	78.7	69.2
Kovar	85.1	83.8	79.4	71.5	67.1

densities on kovar may be due to hindered crystal nucleation.

In electrolyte II (Table 2), the current efficiency for silver at working current densities (1.0–1.5 A dm^{-2}) is somewhat lower than in electrolyte I, possibly because of hydrogen evolution on reaching the limiting diffusion current.

The adhesion strength and porosity of silver coatings deposited on the substrates under study was checked and their microhardness was determined [14].

The adhesion strength was determined by the mark method. Firm adhesion of the coating to the base metal was observed on copper, copper–tin alloy, silver and platinum in the case of deposition from electrolyte I. In electrolyte II, coatings on copper and copper–tin alloy peeled off in some cases. Adherent silver coatings were observed in all cases on nickel substrates. Coatings deposited on kovar both from electrolyte I and from electrolyte II, however, peeled off during checking.

The coatings deposited on copper and copper–tin alloy at current densities of 0.75–1.25 A dm^{-2} from electrolyte I were practically poreless at a thickness of 6–8 μm. The coatings deposited from electrolyte II under the same conditions had pores. Only at higher current densities the average number of pores in the coating obtained from electrolyte I was 3–5 pores cm^{-2}. On nickel and kovar, pores were noted in all cases.

The results of measuring the microhardness of the deposited coatings are summarized in Table 3. One can see that the microhardness of silver coatings deposited at low current densities has close values. At higher current densities (1.0–1.5 A dm^{-2}), the microhardness of the coatings deposited from electrolyte I was somewhat higher than that of the coatings deposited from electrolytes II.

A high corrosion resistance of the coatings deposited from electrolyte I was observed. On keeping coated specimens in air for a year, no change in color and physicochemical properties was noticed, indicating a high corrosion resistance of these coatings.

The service life of electrolyte I in the case of using silver anodes (in jackets) without adjustment is 6 months and with the adjustment of the main constituents about 3 years. The service life of electrolyte II is over 4 years (in case a gold sublayer is used under silver).

In silver plating baths, which are operated for months, potassium carbonates may accumulate, which can be removed with barium cyanide. When their concentration is high, it is necessary to partly replace the bath; therefore, it is easier to extract silver from the solution by any method.

Thus, sound adherent silver coatings with good anticorrosive properties, microhardness and low porosity have been deposited on different substrates (platinum, silver, copper, copper–tin alloy, nickel, kovar) from a BPC electrolyte prepared by method I.

CONCLUSIONS

1. An electrolyte composition and electrolysis conditions have been proposed for depositing functional silver coatings without gold sublayer. Its optimal composition is (g/l): $KAg(CN)_2$ 30–45; K_2CO_3 5–6; K_2HPO_4 8–12; KH_2PO_4 10–15; H_3BO_3 20–25; pH 7 ± ± 0.1, at a temperature of 55 °C.

2. Silver was electrodeposited on various substrates: Pt, Ag, Cu, Cu–Sn (0.15% Sn), Ni, kovar. The effect of current density on the quality, structure and physicochemical properties of silver coatings obtained on various substrates from dicyanoargentate-borate-phosphate-carbonate (BPC) baths has been elucidated. Dependently on the substrate material, the optimal current density for silver electrodeposition is 0.5–1.0 A dm^{-2}.

3. The influence of the bath preparation method on the properties of deposits has been investigated. Sound adherent silver coatings with good anticorrosive properties, microhardness and low porosity have been deposited on different substrates from a BPC bath prepared by method I (bath prepared by using AgCl and potassium ferrocyanide).

4. It has been shown that silver coatings obtained from BPC bath under optimal condition possess desired functional properties to meet the needs of microelectronics industry.

Table 3. **Microhardness of the deposited silver coatings H_v (kG · mm^{-2}) as a function of current density**

Current density, A dm^{-2}	Electrolyte I		Electrolyte II	
	Copper	Nickel	Copper–tin (Sn – 0.15%)	Nickel
0.50	67	70	67	62
0.75	70	70	68	63
1.00	74	71	88	88
1.25	90	82	77	77
1.50	88	60	72	70
2.00	65	50	60	58

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