ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 10, No. 1. 2004

Corrosion Behavior of Electroplated Silver Coatings

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Received 06 October 2003; accepted 26 October 2003

The functional silver coatings were electrodeposited at various current densities from the borate-phosphate-carbonate (BPC) bath on copper and nickel substrates. The morphology of obtained coatings was studied by SEM and STM. Corrosion properties in 0.5 M H_2SO_4 solution was determined by methods of impedance spectroscopy and voltammetry. Corrosion products were determined by EDX analysis.

The corrosion behavior of silver coatings was strongly related to their morphology. A higher corrosion resistance (15.4 kOhm cm^2) was found for silver coatings obtained at lower current density 0.5 A dm^{-2}. These coatings were fine-crystalline, smooth and compact. Upon these data, the operational range of current density (0.4 – 0.6 A dm^{-2}) was established. The studied silver coatings are intended for microelectronics applications.

Keywords: silver, electrodeposition, functional coatings, corrosion behavior.

INTRODUCTION

Currently, the main goal of development highly efficient and economical silver plating technologies is elaboration and industrial application of baths not containing "free" cyanides [1 – 2] or even completely cyanide free solutions, there as a source of silver is e.g. thiocyanate [3 – 4] or sulphite [5] silver complexes.

However, electrodeposition of functional silver coatings for fabrication of electronic devices is performed mainly from solutions, containing $Ag(CN)_x^{1-x}$ complexes as a source of silver. Usually they contain either some amount of free cyanide ions, thiocyanates [2, 6 – 7], or buffer additives. The borate-phosphate-carbonate (BPC) silver plating baths [8 – 10] are considered as alternative to the conventional cyanide baths because: (a) these electrolytes have no excess of free cyanide ions, so are sufficiently less toxic; (b) they enable to obtain adherent coatings with tailor-made functional characteristics such as contact resistance, microhardness, corrosion resistance, and solderability. The required mechanical properties and surface morphology might fit needs of microelectronics industry.

Corrosion of microelectronic devices has been recognised as a major problem for several reasons. For example, the width and separation of thin film metallic lines in integrated circuit devices have been reduced to less than 1 μm. Taking into account the dimensions and voltage involved, the electric fields can reach in access of 100 V/cm. Even a small amount of ionic contamination in the presence of such high fields can totally destroy these devices within a short period of time. A source of ionic contamination can be organic and inorganic compounds widely used in microelectronics. Humidity and high temperatures can easily enhance the types of damages. In addition, during fabrication electronic devices are exposed to the environment, which might be quite hostile. Materials and coatings for devices are mainly selected by their electronic and other functional properties [11]. In the most cases, the selection of materials is based on the properties of bulk material, e.g. metallurgical materials. However, the corrosion behavior of silver depends on the fabrication method, and corrosion rate of bulk and deposited silver could vary up to 10 times dependently on the deposition method [12].

The aim of this work was to investigate the morphology and corrosion behavior in the acid solution of silver coatings obtained from the BPC electrolyte on Cu and Ni substrates at different current densities.

EXPERIMENTAL

Silver coatings were electrodeposited on the copper and nickel specimens from borate-phosphate-carbonate bath. The bath composition was (g l^{-1}): $KAg(CN)_2$ 30 – 45; K_2CO_3 5 – 6; K_2HPO_4 8 – 12; KH_2PO_4 10 – 15; H_3BO_3 20 – 25. The pH value was 7.0 ±0.1 and the bath temperature was 55 ±0.1 °C. The temperature of the solutions was maintained by means of a thermostat UTU-4. The preparation of BPC baths is described in [10]. Before the silver electrodeposition, all specimens were degreased by electrochemical method. Then copper electrodes were treated in a bright pickling solution, rinsed and activated. The nickel specimens were pickled, washed and kept in a citric acid solution.

The deposition was performed at cathodic current densities 0.3 to 2 A dm^{-2}. The thickness of obtained silver coatings was 7 – 8 μm. The morphology of these coatings was assessed from the SEM images obtained by scanning electron microscope LEO-435VP (Germany) and STM images obtained by scanning tunneling microscope NanoScope IIIa made by Digital Instruments.

Electrochemical corrosion measurements of obtained coatings were performed in 0.5 M H_2SO_4 solution at temperature 24 ±1 °C at different current densities. The solution was open to air. The exposed area of the sample was 1 cm^2. Measurements were performed in three-

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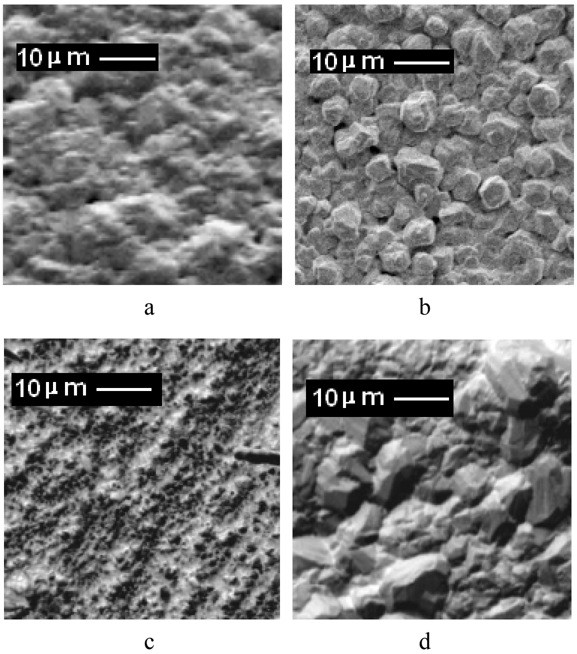
electrode cell with a saturated calomel electrode as the reference, and Pt wire netting as the counter electrode. All potential values are expressed versus the saturated calomel electrode. For comparison the same corrosion tests were performed for metallurgical silver, metallurgical copper and metallurgical nickel.

The corrosion test consisted of impedance spectroscopy and voltammetric measurements. These investigations were carried out using AUTOLAB system (GPSTAT 20 + FRA) with the software GPES 4.9 and FRA 4.9. Electrochemical impedance spectra were measured after stabilization of the open circuit potential (after 15 minutes exposure to the corrosion solution). The amplitude of the sinusoidal voltage was 5 mV and spectra were taken in the frequency range: 50 kHz – 1 mHz. Parameters of the corrosion process were determined upon the analysis of obtained spectra.

Voltammetric measurements were performed on recording of cyclic anodic polarization curve by staircase mode. The potential step was 5 mV and the apparent scan rate was 1 mV/s. Received curves were corrected for the ohmic drop. Parameters of the passive state were estimated from the course of these curves. Corrosion rate was also derived from the analysis of polarization data in the vicinity of the open circuit potential (±50 mV).

RESULTS AND DISCUSSIONS

Obtained coatings were silvery-white color and well adherent. Figure 1 shows SEM images of silver coatings deposited from BPC bath on a copper and nickel substrates at different current densities.



a b

c d

Fig. 1. SEM images of silver coatings deposited on the Cu (a, b) and Ni (c, d) at current densities (A dm^{-2}): 0.5 (a, c) and 0.75 (b, d)

The coatings on copper substrates were dense, uniformly distributed over the surface and homogeneous in structure. The silver deposit obtained at low current densities (0.3 – 0.5 A dm^{-2}) had a homogeneous close-packed fine-crystalline structure.

The coating structure becomes coarser-crystalline with increasing current density. These coatings become highly inhomogeneous and powdered, loose, rough and probably porous. It is typical for deposits obtained under the diffusion limiting current density.

At current densities 0.5 – 0.75 A dm^{-2}, the coatings deposited from the BPC electrolytes on a nickel substrate were loose and inhomogeneous, and individual crystals or groups of crystals were observed on the surface, which may be due to hindered silver crystal nucleation. In more details, the morphology of silver coatings obtained on Cu and Ni substrates are described in [10].

The similar dependence can be observed as well on STM photos (Fig. 2). The roughness of coatings is less 100 nm, and this value is acceptable to apply this process in microelectronics industry.

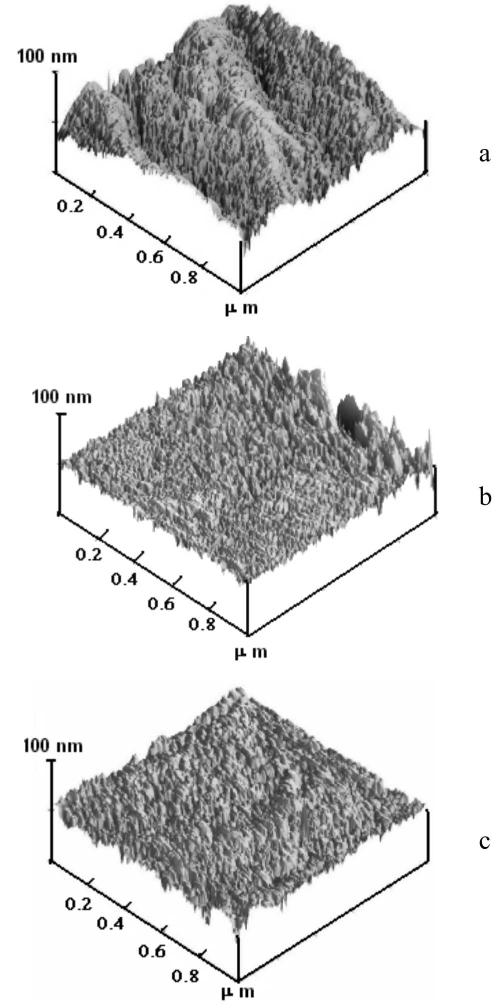


Fig. 2. STM images of silver coatings deposited on the Cu at current densities (A dm^{-2}): 0.3 (a), 0.5 (b) and 0.75 (c)

Results of the corrosion tests revealed the crucial effect of the deposition current density on the corrosion properties of silver coatings. Impedance spectra have a shape of the capacitive arc (Fig. 3) for all samples of silver coatings on copper substrate. The biggest arc was observed for the metallurgical silver. Spectra for the silver coatings lie in between. The biggest size of this arc was registered for silver samples electrodeposited at 0.3 – 0.5 A dm^{-2}, whereas the lowest one was taken for the sample

Table 1. Corrosion parameters for the samples calculated from EIS and voltammetric data

	Cu	Ag coatings on Cu at j, A dm^{-2}			Ag	Ag coatings on Ni at j, A dm^{-2}			Ni
		1.0	0.5	0.3		0.3	0.5	0.75	
R_{ct}, kOhm cm^2	0.1	0.26	4.06	4.95	21.8	0.3	0.3	0.2	0.37
R_p, kOhm cm^2	0.4	0.14	15.4	5.02	19.9	0.32	0.21	0.2	1.89

Table 2. Corrosion parameters for the silver coatings as a function of deposition conditions calculated from voltammetry data

Samples			Corrosion potential, V	Corrosion current, A	Corrosion rate, mm year^{-1}
Ag metallurgical			–0.005	$1.08\ 10^{-6}$	$3.52\ 10^{-3}$
Cu metallurgical			–0.018	$2.26\ 10^{-5}$	$4.00\ 10^{-2}$
Ni metallurgical			–0.279	$8.95\ 10^{-5}$	$2.93\ 10^{-1}$
Ag coating electrodeposited at j, A dm^{-2}	on Cu	0.3	0.040	$4.04\ 10^{-6}$	$1.32\ 10^{-2}$
		0.5	–0.019	$8.40\ 10^{-7}$	$2.75\ 10^{-3}$
		0.75	0.021	$1.14\ 10^{-4}$	$3.74\ 10^{-1}$
		1.0	0.011	$9.40\ 10^{-5}$	$3.07\ 10^{-1}$
	on Ni	0.3	–0.261	$3.59\ 10^{-5}$	$1.17\ 10^{-1}$
		0.5	–0.274	$8.77\ 10^{-5}$	$2.87\ 10^{-1}$
		0.75	–0.304	$9.07\ 10^{-5}$	$2.97\ 10^{-2}$

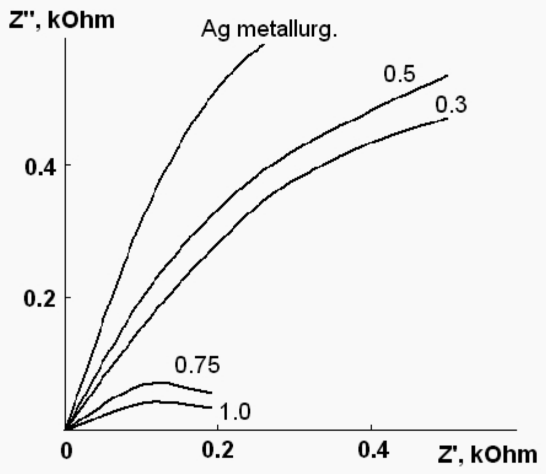


Fig. 3. Nyquist plot for the metallurgical silver and silver coatings electrodeposited from the BPC bath on Cu substrate at various current densities (indicated next to curves in A dm^{-2})

deposited at highest current density. As it can be seen, the size of the arc decreases with increasing current densities of electrodeposition. These impedance data can be described by a parallel combination of the charge transfer resistance R_{ct} and the constant phase element CPE for the description of the double layer (Fig. 4). Based on the obtained spectra analysis, impedance parameters of the charge transfer process were determined. The calculated values of the charge transfer resistance are shown in Table 1.

As it could be expected, the coatings obtained at 0.3 and 0.5 A dm^{-2} exhibit higher values of the R_{ct} than coatings deposited at 1.0 A dm^{-2}. The findings indicate a higher corrosion resistance of coatings prepared at lower current densities. However, comparison of the relevant values of R_{ct} suggests a lower corrosion resistance of silver coatings than that for metallurgical Ag.

Increase in size of the arc corresponds to the higher charge transfer resistance and, subsequently, to the lower rate of corrosion.

Polarization curves for the tested coatings, pure Ag and Cu are presented in Fig. 5. There are evident differences in the course of the curves at lower overpotentials. The patterns for silver coating obtained at 0.5 A dm^{-2} and pure Ag are similar. The highest dissolution currents were observed for silver coatings deposited at 0.75 and 1.0 A dm^{-2}. The curve for coatings obtained at 0.3 A dm^{-2} is shifted to more positive potentials. This probably related to the porosity of coatings and effect of substrate.

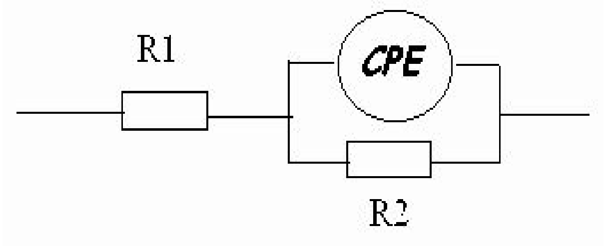


Fig. 4. The equivalent circuit used to fit the impedance spectra (R_1 – solution resistance, R_2 – charge transfer resistance, CPE– constant phase element)

The calculated corrosion parameters are presented in Table 2. These data well correlate with the charge transfer resistance presented in Table 1.

The composition of corrosion products was identified by means of EDX analysis. It was found that it is mainly composed of silver sulphate Ag_2SO_4 (Table 3).

Table 3. EDX analysis of composition of the corrosion products of the coating surface

Samples, electrodeposited at j (A dm^{-2})	C, at.%			
	Ag	Cu	O	S
0.5	71.15	0.54	23.57	4.74
1.0	66.86	10.45	18.36	4.34

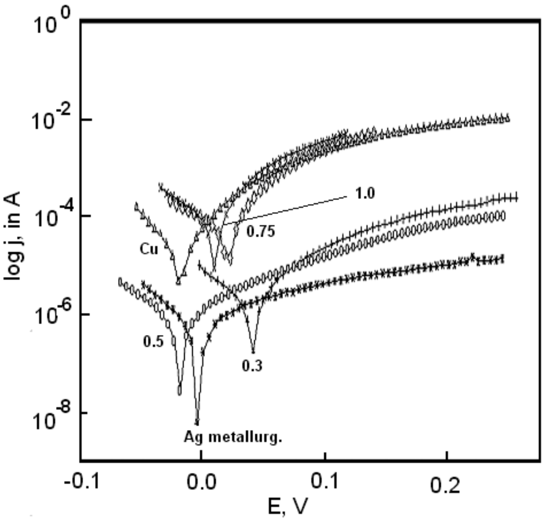


Fig. 5. Polarization curves for the metallurgical silver, copper and silver coatings electrodeposited on Cu substrate at various current densities (A dm^{-2}), that values are marked below the curves

Adhesion strength and porosity of silver coatings deposited on the substrates under study had been performed, and the microhardness has been determined [6]. Taking into account these results it can be stated that adherent silver coatings with the best anticorrosive properties, microhardness and low porosity can be deposited on copper substrates from a BPC electrolyte at current densities 0.5 A dm^{-2}.

CONCLUSIONS

1. Correlation between morphology of the deposited coatings and their corrosion behavior in sulfuric acid is shown. The coatings electrodeposited on a copper substrate at current density 0.3 – 0.5 A dm^{-2} are stable to corrosion. Their corrosion characteristics (corrosion resistance, corrosion current, and corrosion rate) are close to the metallurgical silver. However, corrosion characteristics are worse as compared to the metallurgical silver. Coatings electrodeposited at higher current densities (0.75 A dm^{-2} and higher) show low corrosion stability. Probably, the substrate material effects on corrosion current values.
2. Influence of substrate material on its corrosion properties becomes more evident with increasing of non-uniformity and porosity of coatings. The influence of the substrate on the corrosion characteristics is especially noticeable in series of galvanic coatings obtained on nickel: coatings obtained on nickel are not corrosion stable.
3. The analysis of EDX spectra shows an increase the influence of substrate material on coatings with increase of current density during deposition.

Acknowledgments

Authors are grateful to Ukrainian State Foundation for Fundamental Research under Ministry of Education and Science (grant No. 03.07.117). In addition, O.Bersirova thanks for a fellowship from the Polish Foundation Kasa Mianowskiego.

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DOI: 10.5755/j02.ms.26591