Corrosion Behavior of Electroplated Silver Coatings

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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 H₂SO₄ solution was determined by methods of impedance spectroscopy and voltammetry. Corrosion products were determined by EDX analysis.

Corrosion behavior of silver coatings was strongly related to their morphology. A higher corrosion resistance (15.4 kΩm²) 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⁻zung complext 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; K₂CO₃ 5 – 6; K₂HPO₄ 8 – 12; KH₂PO₄ 10 – 15; H₂BO₃ 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 H₂SO₄ solution at temperature 24 ±1 °C at different current densities. The solution was open to air. The exposed area of the sample was 1 cm². Measurements were performed in three-
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 $0.5 - 0.75 \text{ A dm}^{-2}$, 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].

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.

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 ($0.3 - 0.5 \text{ A dm}^{-2}$) had a homogeneous close-packed fine-crystalline structure.

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 ($\pm 50 \text{ mV}$).

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 $0.3 - 0.5 \text{ A dm}^{-2}$, whereas the lowest one was taken for the sample
Table 1. Corrosion parameters for the samples calculated from EIS and voltammetric data

| Samples | Ag coatings on Cu at \( j \), A dm\(^{-2} \) | Ag coatings on Ni at \( j \), A dm\(^{-2} \) | | Cu | 1.0 | 0.5 | 0.3 | Ag | 0.3 | 0.5 | 0.75 | Ni | 0.2 | 0.3 | 0.2 | 1.89 |
|---------|---------------------------------|---------------------------------|---|-------|---|-------|---|-------|---|-------|---|-------|---|-------|
| \( R_{ct} \), 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

<table>
<thead>
<tr>
<th>Samples</th>
<th>Corrosion potential, V</th>
<th>Corrosion current, A</th>
<th>Corrosion rate, mm year(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag metallurgical</td>
<td>-0.005</td>
<td>1.08 ( 10^{-6} )</td>
<td>3.52 ( 10^{-3} )</td>
</tr>
<tr>
<td>Cu metallurgical</td>
<td>-0.018</td>
<td>2.26 ( 10^{-3} )</td>
<td>4.00 ( 10^{-2} )</td>
</tr>
<tr>
<td>Ni metallurgical</td>
<td>-0.279</td>
<td>8.95 ( 10^{-5} )</td>
<td>2.93 ( 10^{-1} )</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Samples, electrodosed at ( j ) (A dm(^{-2} ))</th>
<th>C, at.%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ag</td>
</tr>
<tr>
<td>0.5</td>
<td>71.15</td>
</tr>
<tr>
<td>1.0</td>
<td>66.86</td>
</tr>
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</table>
Acknowledgments

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REFERENCES