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COMPARATIVE CHARACTERIZATION OF ELECTROCHEMICALY DEPOSITED GOLD DECORATIVE COATINGS

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ABSTRACT
The aim of this work was comparative characterization of electrochemically deposited gold decorative coatings obtained from the freshly synthesized electrolyte, then from the electrolyte aged for a year and coatings obtained from the electrolyte obtained by dissolving crystals of gold-mercaptotriazole. External appearance of the coatings, thickness, surface roughness, the Knoop microhardness and electron microscopy - SEM with EDS showed that the coatings obtained from all the three electrolytes are bright and with good adhesion. The smallest roughness was measured for the coating obtained from fresh electrolyte and the greatest for the coating obtained from electrolyte obtained by dissolving crystals. In terms of hardness there are no significant differences.
Key words: comparative characterization, external appearance, thickness, surface roughness, the Knoop microhardness, SEM with EDS

1. INTRODUCTION
The electrodeposition of gold is a key technology in the industry of microelectronic, optoelectronic and microsystem devices [1-3]. The gold coatings can be broadly classified into two categories: soft gold and hard gold. Soft gold can be plated from non-cyanide baths but hard gold can be plated only from traditional cyanide baths [4].
Soft gold, is used for electronic packaging, such as fabrication of interconnects in integrated circuits (ICs), or forming connections to external devices, using tape automated bumping (TAB) or chip-on-glass (COG) and chip-on flex (COF) techniques [5-9]. Hard gold is used as a contact material for electrical connectors and printed circuit boards (PCBs), relays and switches, which should be resistant to mechanical wear whilst having a low electrical contact resistance [10-11].
Traditionally, gold has been plated from gold cyanide electrolytes. The cyanide bath is exceptionally stable with the stability constant of AuCN being 10^{38}. However, due to concerns about safety and disposal of process waste, there is growing concern regarding the use of cyanide based processes [10].
The interest in developing non-toxic gold electrolytes, such as those based on sulfite complexes, has grown rapidly in recent years. The most common non-cyanide gold electrolyte is based on a gold-sulfite complex, which has problems related to stability and resist compatibility [10-11].
A new electrolytic bath based on gold complex with mercaptotrizole, developed and tested at the Institute of Mining and Metallurgy Bor, can be successfully used in electrolytic baths for hard and decorative gold plating [11]. It was found that the decorative gold coatings obtained from electrolyte based on mercaptotriazole are of a acceptable quality. They are of the same thickness and similar surface roughness as those obtained from commercial cyanide electrolyte. Furthermore, their thickness is more uniform which points to a good throwing power of this organic complex in spite of an absence of any other additives for flatness [11-12].

2. EXPERIMENTAL

Decorative gold coatings were obtained by electrochemical deposition from gold complex based on mercaptotriazole at optimal ooperation conditions [11] from the freshly synthesized electrolyte, then from the electrolyte aged for a year and coatings obtained from the electrolyte obtained by dissolving crystals of gold-mercaptotriazole. Before insertion into the electrochemical cell, the brass substrates were prepared [13].

Characterization of the coatings was performed by checking external appearance, thickness, surface roughness, the Knoop microhardness and electron microscopy - SEM with EDS.

Checking the external appearance was carried out visually. The coating thickness was measured using an apparatus of type UPA XRF 200 A by means of X-ray reflection from gold atoms. The apparatus operates with an error that is a function of coating thickness. Decorative gold coating roughness was determined using a Surface Roughness Tester TR200 device. The measurement results are read via computer, using the TR200 Time Data View software according to the DIN EN ISO 4287 (1998) standard measuring the parameters [13]. The following parameters were measured: R_a - arithmetical mean deviation of profile; R_q - root-mean-square deviation (RMSD) of profile; R_z - ten-point height of irregularities; R_y - maximum height of profile; R_t - total peak-to-valley height; R_p - maximum height of profile peak; R_m - maximum depth of profile valley; S - mean spacing of local peaks of profile; S_m - mean spacing of profile elements; S_k - skewness of the profile [13]. Microhardness of gold coatings, obtained from the three different electrolytes, was measured using the apparatus type Kleinhärter prüfen fur Vickers, Knoop, und Ritzhärte produced by LEITZ 2 using the Knoop method (HK) with 25 N loading. All hardness values were reported in the Knoop (HK) scale. The morphology of gold coatings, obtained from all the three electrolytes, was studied using a scanning electron microscope (SEM model: JOEL JSM-6610LV operated at 20 keV). Chemical composition of the gold coatings was determined using energy dispersive X-ray spectroscopy (EDS). The EDS spectra for gold coatings were recorded using the X-ray spectrometer attached to the scanning electron microscope.

3. RESULTS AND DISCUSION

3.1 External appearance

From the visual appearance of decorative gold coatings, obtained from fresh electrolyte and the aged electrolyte it can be concluded that the coatings obtained from both electrolytes are bright and uniform and fully meet the requirements of decorative gold plating (standard SRPS ISO 4523: 1992) [14]. Coating obtained from electrolyte obtained by dissolving crystals of the complex of gold with mercaptotriazole is also bright and uniform, but the coating was darker on the edges of the sample.

3.2 Gold thickness

The value of measured thickness of coatings obtained from all the three electrolytes are shown in Table 1.

Table 1. Measured thickness of decorative gold coatings obtained from three different electrolytes

	Fresh electrolyte	Aged electrolyte	Electrolyte obtained by dissolving of Au-MT
Gold thickness (μm)	0.08±0.012	0.07±0.012	0.06±0.011

Thickness of gold coatings, obtained with the same quantity of electricity, from fresh electrolyte was 0.08±0.012 μm, from aged electrolyte it was 0.07±0.012 μm and from electrolyte obtained by dissolving of Au-MT crystals was 0.06±0.011 μm (Table 1). Coatings obtained from all the three electrolytes fully meet the requirement of decorative coatings in terms of the thickness [13].

3.3 Surface roughness

The measured surface roughness parameters of the decorative gold coatings given in Table 2 show that:

- surface roughness is the smallest for gold coating obtained from fresh electrolyte (R_a = 0.0535 μm) and the highest for the coating obtained from electrolyte obtained by dissolving of Au-MT (R_a = 0.0655 μm).
- surface roughness of gold coating obtained from aged electrolyte was 0.0555 μm.

Table 2. Surface roughness parameters of gold coatings obtained from three different electrolytes

	Fresh electrolyte	Aged electrolyte	Electrolyte obtained by dissolving of Au-MT
R_a (μm)	0.0535	0.0555	0.0655
R_q (μm)	0.071	0.07	0.1055
R_z (μm)	0.067	0.0515	0.1565
R_y (μm)	0.273	0.23	0.581
R_t (μm)	0.72	0.4395	1.78
R_p (μm)	0.1335	0.0795	0.4115
R_m (μm)	0.1395	0.15	0.1695
S (mm)	0.2333	0.09885	0.68565
S_m (mm)	0.7222	0.8333	0.75755
S_k	1.5715	-0.702	7.7705

3.4 Microhardness of gold coatings

Each sample was subjected to hardness measurements at three different locations (left and right edges of the sample and intersection of diagonals).

The values for all three measurements and the average value of three measurements is shown for each sample in Table 3.

Table 3. Microhardness of gold coatings obtained from three different electrolytes

HK	Fresh electrolyte	Aged electrolyte	Electrolyte obtained by dissolving of Au-MT
HK_{sr} (MPa)	665	640	622
HK_1 (MPa)	675	645	614
HK_2 (MPa)	670	636	636
HK_3 (MPa)	650	639	616

From Table 3, it can be concluded that the highest mean value of microhardness was measured for the coating obtained from fresh electrolyte (HK_{sr} = 665 MPa). The microhardness of the coating obtained from aged electrolyte was HK_{sr} = 640 MPa and the minimum value of microhardness was measured for the coating obtained from the electrolyte obtained by dissolving crystals of auri-mercaptotriazole (HK_{sr} = 622 MPa). The measured microhardness values were correlated with the thickness of the coating.

3.5 SEM with EDS

The chemical composition of the gold coatings obtained from fresh electrolyte, aged electrolyte and electrolyte obtained by dissolving of crystalline Au-MT shown in Table 4, was determined by means of EDS.

From the SEM image of the decorative gold coatings obtained from all the three investigated electrolytes, it can be concluded that the coatings are bright and adherent. The chemical composition of the gold coatings, presented in Table 4, show the presence of nickel in all three samples, because the gold coatings are very thin (0.06-0.08 μm thickness), so the electrons can pass through the coating and penetrate into the nickel substrate. The chemical analysis also showed the presence of copper and zinc from brass samples. The content of gold in the coating obtained from fresh electrolyte was the highest (64.64%) and it was the lowest in coating obtained from electrolyte prepared by dissolving crystals (50.45%). In the coating obtained from the aged electrolyte the content of gold was 61.15%. These results are in agreement with the thickness of coatings obtained from the three kinds of electrolyte.

Table 4. Chemical content (EDS) of gold coatings obtained from three different electrolytes

Element %	Fresh electrolyte	Aged electrolyte	Electrolyte obtained by dissolving of Au-MT
Ni	29.96	33.43	46.13
Cu	2.18	3.35	2.31
Zn	3.22	2.07	1.11
Au	64.64	61.15	50.45
Σ	100.00	100.00	100.00

4. CONCLUSION

Comparative characterization of electrochemically deposited decorative gold coatings obtained from the freshly synthesized electrolyte, then from the aged electrolyte and coatings obtained from the electrolyte obtained by dissolving crystals of gold-mercaptotriazole showed that all those coatings are bright and uniform and fully meet the requirements of decorative gold plating in the terms of thickness, surface roughness, microhardness and external appearance.

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