

Investigation of the structure of copper coatings obtained by chemical deposition from formaldehyde-free solution on dielectrics

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Copper coatings are obtained by chemical deposition from formaldehyde-free, weakly alkaline copper plating bath, which is non-toxic and non-aggressive to a large part of the dielectrics. The present paper reports the results from investigations of the morphology, microstructure and micro-texture of the copper coatings. The influence of the concentration of Cu^{2+} ions and reducing agent ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$) as well as pH, temperature and deposition time on the thickness of the copper coatings is studied. The chemical composition of the coatings is defined using EDS analysis. The thickness of the copper coatings is determined by XRF analysis. Morphology of the coatings is examined by scanning electron (SEM) and optical microscopy. The obtained copper coatings could find application as layers on metal and non-metal samples, in the production of new materials for the electronics, energetics, fine mechanics, optics and printed circuit boards with covered holes.

Keywords: chemical deposition, copper coatings, formaldehyde-free, weakly alkaline solution, microstructure, dielectrics

INTRODUCTION

Chemical copper plating is widely used for deposition of copper layers on various dielectric materials and semiconductors in order to obtain decorative and functional properties. The copper coatings are widely used in electronics for formation of conductive images or opening holes in the production of printed circuit boards and integrated circuits [1-5]. Formaldehyde or its derivatives are traditionally used reducing agents in solutions for chemical copper deposition because of the excellent mechanical properties of the deposited copper coatings and their high deposition rate [6, 7]. Unfortunately, these solutions exhibit some disadvantages [8, 9]. One of them is that the catalytic oxidation of the formaldehyde increases with increasing hydroxide concentration and by this reason, these solutions are effective at pH above 11. However, the high pH is incompatible with some dielectric materials and photo-resists used in the photolithography processes. For this reason, the research in this topic is focused at development chemical copper solutions that do not contain formaldehyde or its derivatives [10-14]. Alternative reducing agents are proposed as follows: borohydride [15], Co (II) [16], sodium hypophosphite [17-22] and others. Among them, sodium hypophosphite is an attractive reducing agent because the final solutions are relatively inexpensive and safe to use. However, sodium hypophosphite is widely used as a reducing agent in

the chemical deposition of some metals such as nickel or cobalt, but not in copper deposition. The reason is that its reducing ability is not catalyzed by the copper [16-19]. A way to compensate the poor catalytic activity of copper is to add nickel ions to the solution. As a result, a joint deposition of the both metals occur with a minimum amount of nickel into the copper coating. The role of the nickel is to catalyze the oxidation of sodium hypophosphite and to maintain the continuous deposition of copper, depending on the molar ratio of $\text{Ni}^{2+}/\text{Cu}^{2+}$ [23].

The deposition of copper layers from such solutions is well discussed in the literature, however there is no detailed studies on the influence of working conditions and the major components of the solution on their morphology.

The purpose of the present work is to investigate the process of chemical copper deposition from formaldehyde-free copper bath with reduced alkalinity. Sodium hypophosphite is used as a reducing agent in the copper bath. The influence of its concentration, the concentration of copper ions in the solution, pH, temperature and duration of deposition on the morphology, microstructure and micro-texture of chemically deposited copper coatings is studied. The optimal conditions for use of this non-toxic and slightly aggressive copper bath are established.

EXPERIMENTAL

Novodur PM/2C type ABS (Acrylonitrile-

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butadiene-styrene, manufactured by Bayer, Germany) sample with an area of 0.1 dm² was used as substrate. Before deposition, the ABS substrates were preliminary treated by using the technological scheme shown in Fig. 1 [24-25].

The electroless copper plating solution used was with the following composition: CuSO₄·5H₂O as copper ion source and sodium hypophosphite as reducing agent. Their concentrations were varied within the limits according to Table 1. In addition, the following compounds were added to the solution: sodium citrate (16 g L⁻¹) as

The diffraction patterns of the samples were recorded on multipurpose diffractometer system Epyrean (PANalytical) equipped with a multichannel detector (Pixel 3D), Cu anode and operated at 45kV-40mA. Phase analysis and calculation of the crystallites size and micro strains were performed in HighScore (Plus) software version 4.5 (2016), by PANalytical B.V., Almelo,

The Netherlands. The morphology of the coatings was defined by Scanning Electron Microscopy (SEM, JEOL JSM 733, Japan) images. The elemental composition was analyzed by Energy Dispersive Spectroscopy (EDS) /INCA/. The surface roughness of the ABS details was measured by AFM analysis (Nano Scope V system - Bruker Ltd, Germany).

RESULTS AND DISCUSSION

1. X-ray structural studies

The obtaining of chemically deposited copper coatings with certain physical-mechanical properties, such as fine dispersion, hardness, elasticity, internal tensions, etc., depends on their crystal structure. In this regard, in order to identify the factors that influence these properties, it is important to carry out systematic studies of the shape, location, size of the grains and their preferential orientation, depending on

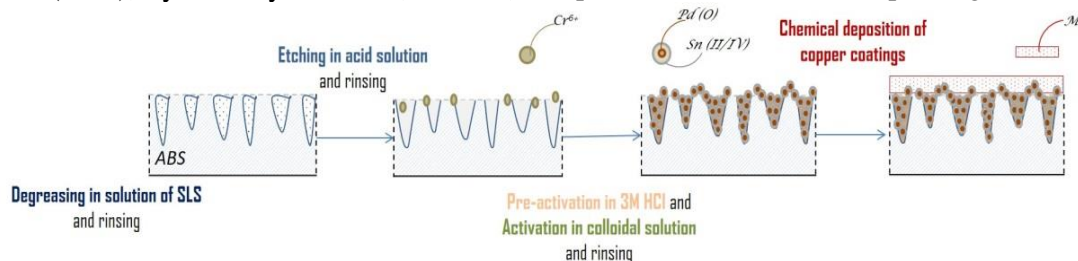


Fig. 1. Technological scheme for preliminary treatment of ABS substrates

complexing agent and boric acid (30 g L⁻¹) as buffer solution. The pH was adjusted using 10M NaOH or H₂SO₄ to a final value of 8.0 to 10.0. The temperature was kept in the range of 50 to 70 °C, and the deposition time was in limits from 5 to 30 min. The plating was performed in 250 ml electroless copper solution with continuous stirring.

The thickness of the copper coatings is determined by XRF analysis (XRF - Fischerscope HDAL). The microstructural parameters of the copper deposits were investigated using X-ray diffraction (XRD), the conditions of chemical deposition of the copper layers. In literature, information about such studies is useful but rather poor [26-27].

In order to identify the relationship between the deposition conditions and the structural characteristics of the layers obtained, a full-profile fitting method was used. The diffraction patterns of the samples were recorded in an appropriate mode in order to determine the parameters of the lattice, the average crystallites size and the strains after each change in the solution composition and the deposition regime. The Maud [28-31] and HighScore plus 4.5 [32] programs were used

independently for the calculations. When layers with small thicknesses (small amounts of irradiated volume) were used, only one well-expressed peak of the copper was most commonly observed on the diffraction patterns. Therefore, the data of the lattice parameters and the average crystallites size were calculated only on the basis of this peak. For size-strain standard were used LaB6 and SRM 660c.

The effect of the following factors on the structure and on the thickness of the layers obtained was studied: concentration of Cu²⁺-ions, concentration of the reducing agent (NaH₂PO₂·H₂O), pH, temperature and deposition time. The data are shown in Table 1.

The data for the imperfection of the coatings due to the accumulation of various defects (twins-, points- and linears-) are expressed as strains in percentages and they are obtained using the profile fitting of the diffraction lines.

1.1. Effect of the concentration of Cu²⁺-ions in the solution

In Fig. 2a, the diffraction patterns of deposited copper layers at different concentrations of Cu²⁺-ions in the solution are presented, based on which

in Table 1 the microstructural parameters are determined.

As it is obvious from the data shown in Fig. 2a and Table 1, changing the concentration of copper sulfate in the range from 1 to 10 g L⁻¹ and

maintaining the ratio between the other components leads to an increase in the size of the elementary building blocks of the copper coating and to an acceleration of its growth.

Table 1: Dependence of the microstructural parameters and the thickness of the copper coating on the concentration of Cu²⁺-ions and the reducing agent in the solution, the temperature, the pH and the deposition time

	Lattice parameter <i>a</i> , [Å]	Crystallite size <i>D</i> , [nm]	Micro Strain <i>ms</i> , [%]	Thickness of the copper coatings <i>δ</i> , [μm]
Concentration of CuSO₄·5H₂O, g L⁻¹ (first column)				
1	3.6216(4)	10,1	0.936(3)	1.16
10	3.6188(3)	65,4	0.192(2)	1.93
30	3.6177(2)	43,8	0.262(4)	0.62
50	Coating consisting most probably of a mixture of Cu ₂ O and CuO			0.63
Concentration of NaH₂PO₂·H₂O, g L⁻¹ (first column)				
1	An amorphous coating consisting most probably of copper			0.33
10	An amorphous coating consisting most probably of a mixture of Cu and Cu(OH) ₂			0.39
30	3.6188(3)	65,4	0.192(2)	1.93
50	3.6193(5)	18,2	0.044(5)	0.59
pH of the solution (first column)				
8.0	3.6059(3)	14,9	-0.067(1)	0.37
8.5	3.6140(4)	20,3	-0.068(2)	0.78
9.0-9.3	3.6188(3)	65,4	0.192(2)	1.93
9.5	3.6142(2)	25,1	-0.063(4)	1.27
10.0	3.6154(3)	75,9	0.147(3)	1.25
Temperature of the solution, °C (first column)				
50	3.6241(2)	9,2	0.066(3)	0.51
60	3.6098(2)	19,5	0.134(4)	0.57
70	3.6188(3)	65,4	0.192(2)	1.93
80	3.6081(3)	26,3	0.266(5)	0.54
Deposition time, min (first column)				
5	3.6201(4)	42,0	0.142(3)	0.70
10	3.6146(2)	24,2	0.131(2)	0.71
20	3.6188(3)	65,4	0.192(2)	1.93
30	3.6107(2)	18,6	0.257(4)	0.82
Air stirring of the solution (first column)				
Without	2.0974(2)	65,3	0.193(4)	0.59
With	3.6188(3)	65,4	0.192(2)	1.93

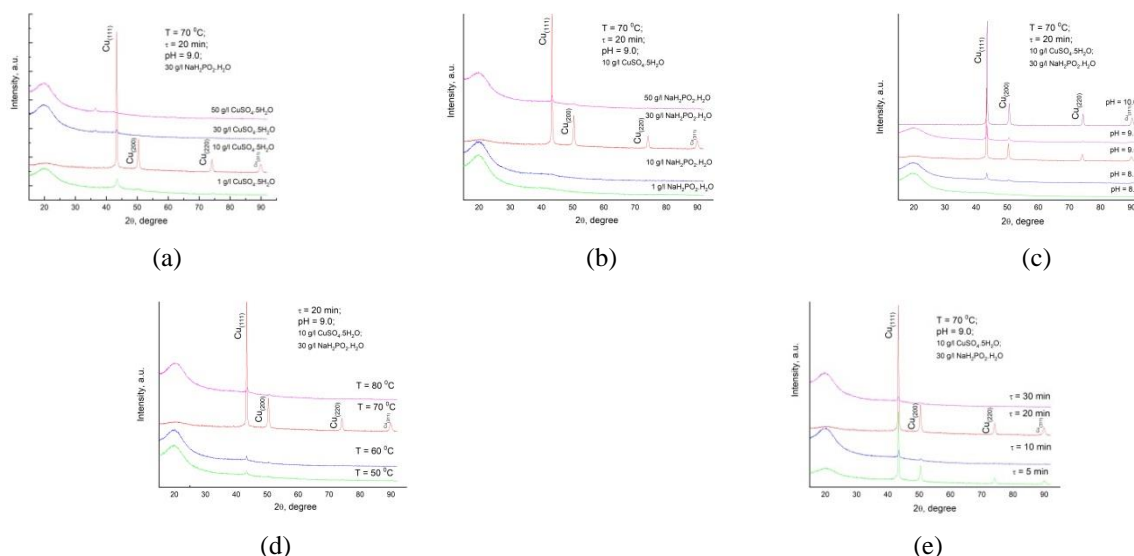


Fig. 2: XRD-pattern obtained at different: a) concentrations of copper sulfate in the solution; b) concentrations of sodium hypophosphite in the solution; c) pH values of the copper solution; d) temperatures of the solution; e) deposition times.

The change in the concentration of copper sulfate in this range also leads to an increase of the size of the crystallites, as well as to an around three-fold increase in the thickness of the coating. The internal strains in the coating increase in proportion to the increasing concentration of the copper ions. Further increase in the concentration of the basic salt to above 10 g L^{-1} leads to a significant decrease in the thickness of the coatings, and at 50 g L^{-1} , a coating, most probably consisting of a mixture of Cu_2O and CuO , is even observed. The results reveal that the deposition process is limited primarily by the diffusion of the copper ions, respectively complexes, and a concentration of 10 g L^{-1} of copper sulfate can be considered optimal (all subsequent studies have been conducted with this concentration).

1.2. Influence of the concentration of the reducing agent (sodium hypophosphite) in the solution

In Fig. 2b, the diffraction patterns of deposited copper layers are shown. They are obtained by varying the concentration of the reducing agent ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$) in the solution and keeping the ratio between the other components. The data for the microstructural parameters are summarized in Table 1.

The analysis of the obtained data shows that as the concentration of $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ in the solution increases to 30 g L^{-1} , the size of the copper crystals forming the coating increases significantly, after which it decreases. Moreover, at low reducing agent concentrations of up to 10 g L^{-1} , amorphous coatings are observed, most likely consisting of a mixture of Cu and $\text{Cu}(\text{OH})_2$. These effects are probably related to the change in the effective concentration of the reducing copper ions near the active centers. At concentrations of the reducing agent higher than 30 g L^{-1} , diffusion restrictions begin to emerge with respect to the delivery of the reducing copper ions and as a result, the size of the growing crystallites decreases.

As the concentration of the reducing agent increases, the internal strains increase too, although to a lesser extent. Based on the analysis of the results, an optimal level of concentration of the reducing agent of 30 g L^{-1} is determined.

1.3. Influence of the pH of the solution

In Fig. 2c, the diffraction patterns of deposited copper layers at different pH values of the solution are shown, on the basis of which the

microstructural parameters were calculated (Table 1).

As seen from the obtained data, the diffraction pattern is clear, unambiguously confirming the quality of the layers obtained. As the pH of the copper electrolyte increases, a gradual increase in the intensity of the peaks and narrowing of their profile is observed. After the processing of the diffraction patterns, the data show that as the pH increases, the lattice parameters begin to approach the equilibrium parameters for Cu , measured at 296 K ($a = 3.6140 \text{ \AA}$) [ICSD:627113, ICDD:98-062-7113], and the crystallites size increases almost twice. As can be seen in the Table 1, the internal strains increase too, though insignificantly. The chosen alkalinity of the solution at which the tests are performed is $\text{pH} = 9.0\div 9.3$.

1.4. Influence of the temperature of the solution for chemical copper plating

The effect of the temperature of the solution on the quality of the coatings was monitored using XRD analysis. The—diffraction patterns are presented in Fig. 2d, and the results of the profile analysis are summarized in Table 1.

As the temperature of the solution increases, an approximation of the lattice parameter of the deposited copper to the equilibrium parameter ($a = 3.6140 \text{ \AA}$) [ICSD:627113, ICDD:98-062-7113] is observed, and the size of the crystals increases significantly, which is accompanied by an increase in the internal strains. The temperature also has a favorable effect on the deposition rate of the copper coating, which rises almost three times in the range of $50\text{-}70 \text{ }^\circ\text{C}$. On the basis of the obtained results, temperature of $70 \text{ }^\circ\text{C}$ is chosen as optimal one.

1.5. Influence of the deposition time for chemical copper plating

The effect of the deposition time on the quality of the coatings was evaluated using XRD analysis. The diffraction patterns are presented in Fig. 2e, and the results of the profile analysis are summarized in Table 1.

As seen from the data shown in Fig. 2e and Table 1, the diffraction pattern is clear, unambiguously confirming the quality of the layers obtained. A gradual increase in the intensity of the peaks and narrowing of their profile at longer deposition times is observed.

All investigations were performed with the use of air stirring, as from the obtained results shown in Table 1 it can be concluded that when applying air

stirring of the solution (air flow at a rate of 100ml/min in 250 ml of solution), the crystalline size remains the same, but the thickness of the copper coating is much higher.

2. Electron-microscopic studies

Figure 3 shows the morphology of a chemical copper coating deposited from formaldehyde-free solution at different pH values.

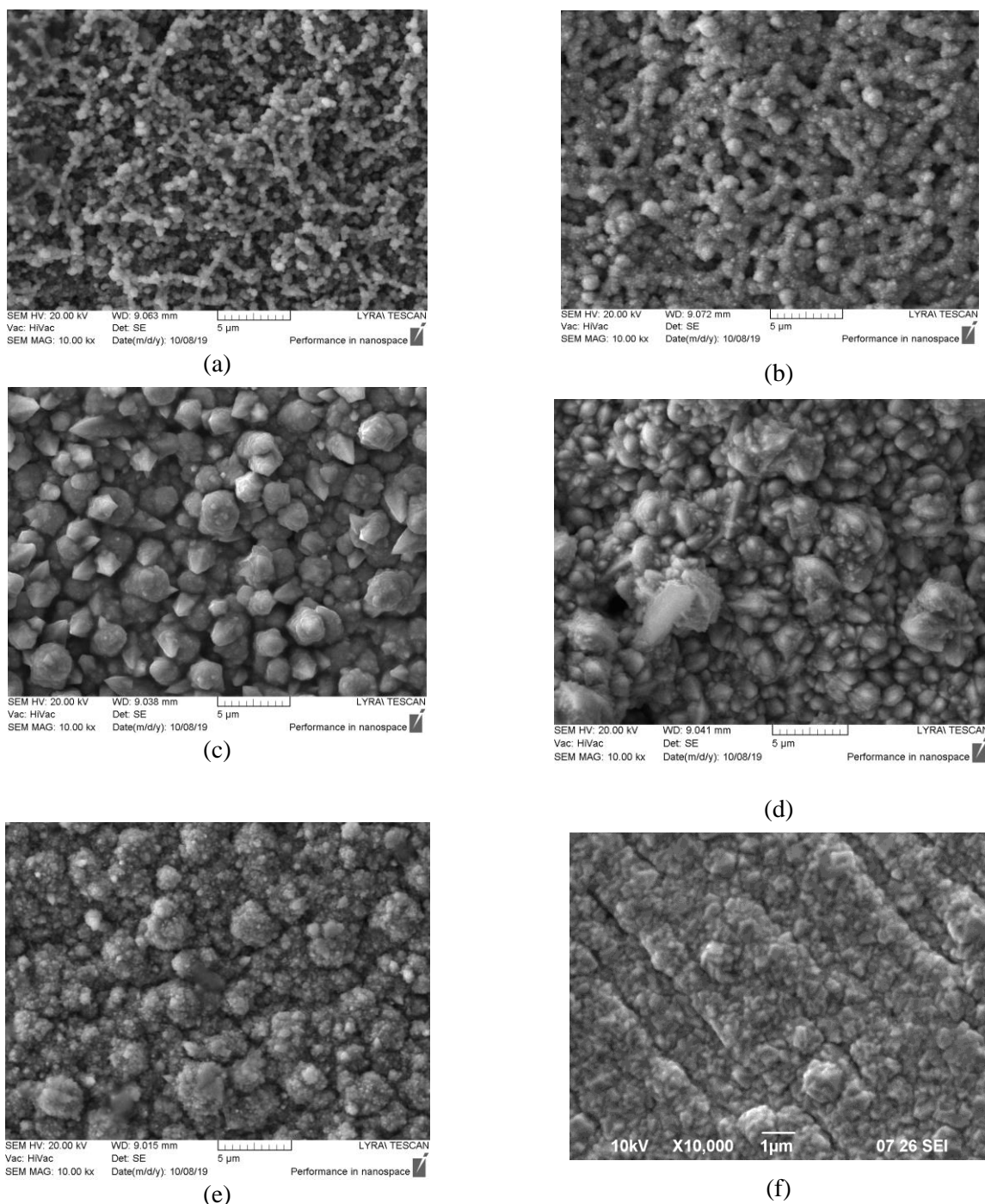


Fig. 3: SEM images of the surface of a chemical copper coating deposited in a formaldehyde-free copper bath at: a) pH =8.5($\tau_{\text{deposition}} = 20$ min); b) pH = 9.5($\tau_{\text{deposition}} = 20$ min); c) pH = 9.0($\tau_{\text{deposition}} = 20$ min); d) pH = 10.0($\tau_{\text{deposition}} = 20$ min); e) pH = 9.0($\tau_{\text{deposition}} = 5$ min); f) chemical copper coating deposited in a trilonic solution ($\tau_{\text{deposition}} = 20$ min).

Figure 3 shows that as the alkalinity of the electrolyte increases, the morphology of the copper coatings becomes more uniform and with clearly shaped agglomerates of single crystals. At low pH

values (Fig. 3a, b), a mesh structure with very small-sized particles is observed (0.1 – 0.5 μm).

SEM-images of the typical surface morphology and structure of a chemical copper coatings deposited in the selected optimal formaldehyde-free

solution at two deposition times (Fig. 3 c, e). These images are compared to the morphology of a chemical copper coating deposited in the most commonly used in the practice copper trilonic solution (Fig. 3 f).

As seen, the copper coating obtained from formaldehyde-free solution at a deposition time of 20 min (Fig. 3 c) is built of pyramidal particles with dimensions of ~ 1 - 3 μm . They are evenly spaced on the surface of the polymer. The lines along which the hydrogen, released during the reduction of the copper ions, moved are clearly outlined. At a deposition time of 5 min, the copper coating obtained from formaldehyde-free solution (Fig. 3e) is built from pyramidal particles with dimensions of ~ 0.01 - 0.1 μm , which form agglomerates several times larger in size. This morphology resembles the morphology of the copper coating obtained from the commercial trilonic solution (Fig. 3f).

EDS-analysis of the ABS polymer treated in a copper formaldehyde-free solution with different pH-values and at two deposition times reveals that there is no significant change in the copper content of the layers (Table 2).

As the copper layers obtained are of a small thickness, the presence of other elements in the substrate is excluded.

3. Roughness

AFM-studies were performed regarding the roughness of not treated ABS sample and treated ABS sample by: chemical copper deposition in a formaldehyde-free solution under the optimal conditions determined by XRD- and SEM-analyzes and by chemical copper deposition in a commercial high-alkaline trilonic solution (Fig. 4). After chemical metallization, the treated samples show considerably greater

Table 2: EDS analysis of ABS polymer treated in a copper formaldehyde-free solution with different alkalinity (pH) and at two deposition times

Sample	Plating composition		
	Wt.%Cu	Wt.%Ni	Wt.%P
pH = 8.5; τ = 20 min	86.89	4.22	0.27
pH = 9.0; τ = 5 min	88.76	4.70	0.52
pH = 9.0; τ = 20 min	89.78	3.31	0.14
pH = 9.5; τ = 20 min	90.29	3.11	0.12
pH = 10.0; τ = 20 min	89.06	4.68	0.26

roughness than that of the not treated sample. The roughness values are as follows: not treated sample

- Ra = 28.95 nm; a sample chemically metallized in a formaldehyde-free solution - Ra = 460.02 nm; a sample chemically metallized in a commercial trilonic solution - Ra = 174.23 nm.

CONCLUSIONS

The influence of the composition and working conditions of a formaldehyde-free copper bath with reduced alkalinity on the morphology, microstructure and micro texture of chemically deposited copper coatings on ABS samples is studied by X-ray structural and electron-microscopic analyzes. The X-ray patterns show that at the optimal concentrations of the components of the solution (10 g.L⁻¹ CuSO₄.5H₂O and 30 g.L⁻¹ NaH₂PO₂.H₂O) and working conditions (pH = 9.0 – 9.3; T = 70 °C; air agitation), the diffraction pattern is clear, unambiguously confirming the quality of the layers obtained. Well pronounced peaks with a narrow profile are observed. The chemically deposited copper layers deposited in a formaldehyde-free copper solution differ significantly from those deposited in a commercial trilonic solution:

- In the case of chemical coatings deposited in a formaldehyde-free copper solution, the crystallites size is 65 nm and the size of the agglomerates is 1-3 μm ;
 - In the case of chemical layers deposited in a trilonic solution, the crystallites size is around 33 nm and the size of the agglomerates is 0.1-0.5 μm .
- Significant differences are also established in the structural parameters of the two types of copper coatings, as well as in their roughness and texture.

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