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Application of environment-friendly ligands for alkaline electroless copper plating systems: A comparative study of electroless copper deposition using D-, L- and DL-tartrate as Cu(II) ligands

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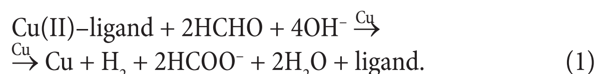
All investigated isomers of tartaric acid, namely L-tartrate, D-tartrate and a racemic mixture of DL-tartrate, forming sufficiently stable complexes with copper(II) ions in alkaline solutions, were found to be suitable ligands for copper(II) chelating in alkaline (pH > 12) electroless copper deposition solutions. Reduction of copper(II)-tartrate complexes by hydrated formaldehyde was investigated and the copper deposits formed were characterized. The thickness of the compact copper coatings obtained under optimal operating conditions in 1 h can reach ca. 3 μm, depending on the temperature and nature of the ligand applied. The plating solutions were stable and no signs of Cu(II) reduction in the bulk solution were observed during the experiment time. Results were compared to those for systems operating with other copper(II) ligands.

Key words: copper, tartaric acid, isomers, electroless copper deposition, surface roughness

INTRODUCTION

Electroless copper plating solutions are widely used in electronics for deposition of metallic copper layers on semiconductors or dielectrics (silicon wafers, resins etc.) [1–2]. Generally the total autocatalytic process of electroless copper deposition is described by the following equation:



$$\text{Cu(II)–ligand} + 2\text{HCHO} + 4\text{OH}^- \xrightarrow{\text{Cu}} \text{Cu} + \text{H}_2 + 2\text{HCOO}^- + 2\text{H}_2\text{O} + \text{ligand}. \quad (1)$$

Copper(II) ligands, along with hydrated formaldehyde as a reducing agent and a copper(II) salt as a copper(II) ions source, are important components of autocatalytic copper deposition systems. Since these systems operate in alkaline milieu, the ligands used must meet several important requirements: these compounds must form copper(II) complexes that are stable enough to prevent precipitation of copper(II) hydroxide, and they should not react with formaldehyde nor retard the catalytic copper(II) reduction reaction.

Ethylenediaminetetraacetic acid (EDTA) is the most widely used ligand in alkaline electroless copper plating baths due to its excelent complexing properties. From the other hand, these perfect chelating properties of EDTA create environmental hazards because of the binding of heavy metal ions into soluble, very stable and hardly decomposable complexes in a wide pH range. In addition, EDTA is very weakly biodegradable. Therefore, the efforts are made to displace the mentioned copper(II) ligand with less hazardous or purely harmless compounds. Such kind attempts are documented when replacing EDTA with other ligands in alkaline electroless copper plating systems. Generally, two classes of chemical compounds were proposed as an EDTA alternative, namely alditols (polyhydroxylic alcohols) and hydroxypolycarboxylic acids.

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Concerning hydroxypolycarboxylic acids, the application of citric acid (2-hydroxypropane-1,2,3-tricarboxylic acid) as a ligand for the alkaline electroless copper plating system has been documented recently [3].

The data on use of tartaric acid (2,3-dihydroxybutanedioic acid) in electroless copper plating as a Cu(II) ligand are not wide-ranging. The general observations and trends are presented in literature [1, 2], whereas the peculiarities of electroless copper deposition from this kind of system were investigated in the last decade [3–7]. It is worth noting that practically all data are obtained at 20–25 °C temperature. The mainly used ligand was L-isomer of tartrate (natural isomer), namely potassium sodium tartrate (Seignette's or Rochele salt), DL-tartrate (racemic mixture of D- and L-isomers) was less applied, whereas the data about using of D-tartrate in electroless copper deposition process are absent.

Therfore, the aim of the work presented herein was a comparative study of the process of electroless copper deposition from alkaline formaldehyde-containing solutions, using different isomers of tartaric acid, namely L- and D-tartrate, and their racemic mixture at different temperatures and pH values.

EXPERIMENTAL

Chemicals and solutions

Analytical grade reagents from Sigma-Aldrich were used, and the formaldehyde source was formalin (37% HCHO) solution. Formaldehyde concentration in the stock solution was determinated iodometrically. Measurements of pH and pH-metric titrations were achieved using a Mettler Toledo MP 220 pH-meter and a Mettler Toledo InLab 410 glass electrode.

Copper surface formation

The substrate was a smooth Pt sheet (1 × 1 cm) electroplated with Cu for 20 min from acid copper solution (1.0 mol l^{-1} $CuSO_4$ + 0.5 mol l^{-1} H_2SO_4) at 1.5 A dm^{-2}. Before the electroless plating, the electroplated substrate was activated for 30 s in acid $PdCl_2$ solution (1 g l^{-1}). The main electroless copper plating experiments were carried out for 30 or 60 min at 10, 20 and 30 °C in 50 ml of the solution containing (mol l^{-1}): $CuSO_4 \cdot 5H_2O$ – 0.05; tartaric acid – 0.15; formaldehyde – 0.15; NaOH – up to pH needed. The amount of copper deposited was determined by the mass difference. All measurements were repeated at least three times and the mean value was calculated.

Determination of the real surface area of the Cu coatings obtained

The copper surface determination method is based on the underpotential deposition of the thallium monolayer on the Cu electrode surface and is described elsewhere [4, 6, 8]. Briefly, the procedure was as follows. The measurements were carried out at 25 °C in 1 mol l^{-1} Na_2SO_4 solution containing 1 mmol l^{-1} $TlNO_3$. Before the measurements copper oxides were removed from the surface: the working Cu electrode was kept at –0.80 V for 5 s. Then the electrode was kept at +0.15 V for 5 s (for dissolving the bulk Tl deposit). A Tl monolayer was formed at –0.49 V for 200 s. Then the Tl monolayer was dissolved using anodic scanning of the potential up to –0.1 V (scanning rate 50 mV s^{-1}). By integration of the potentiodynamic curve obtained (in the range from –0.39 to –0.10 V), the quantity of electricity (Q, μC) used for anodic dissolution of the Tl monolayer was calculated.

The real surface area (in nano-scale dimensions) of the Cu electrode (S_R, cm^2) was calculated using the Tl monolayer capacity Q_{Tl} (the quantity of electricity necessary to form a monolayer on 1 cm^2 of electrode) equal in this case to 112 μC cm^{-2} [8]:

$$S_R = Q/Q_{Tl}. \quad (2)$$

The surface nano-scale roughness factor R_f is calculated as a ratio of real and geometric surface areas:

$$R_f = S_R / S_G. \quad (3)$$

Voltammetric measurements

Voltammetric curves were obtained by the standard electrochemical equipment (potentiostat PI-50, sweep generator PR-8, *xy*-recorder H-307, thermostatted electrochemical cell JES-1 (Belarus) and thermostat UH-4 (Germany)). The solutions were deaerated by Ar. The auxiliary electrode was Pt foil, and the reference electrode was Ag/AgCl with a saturated KCl solution.

Voltammograms of 0.15 mol l^{-1} HCHO were recorded at 20 °C in 0.1 M Na_2SO_4 supporting electrolyte at pH 12.0, 12.5 and 13.0 (solution pH was adjusted by means of NaOH). The Cu electrode was potentiostated at –0.9 V and then voltammograms were recorded in the potential range –0.9 to + 0.1 V (SHE), potential scanning rate being 5 mV s^{-1}. All potentials are presented in reference to the standard hydrogen electrode (SHE).

The mixed potential of the copper electrode (E_{mix}) during the process of electroless copper deposition (the open circuit potential) was measured by means of an xy-recorder H-307 (Russia) using the Ag/AgCl reference electrode with a saturated KCl solution. All potentials are presented in reference to SHE.

Spectrophotometric measurements

Light absorption spectra were recorded using a Perkin Elmer Lambda 35 UV/VIS spectrometer at 20 °C in 1 cm thick quartz cells. The optical blank solution was pure water.

RESULTS AND DISCUSSION

The surface of electroplated Cu electrode

The roughness factor (R_f, i. e. the ratio of real and geometric surface area) of the working electrode electroplated with copper, which was used as a substrate for further electroless

copper plating, was found to be comparatively low and equal to 1.5. It can be noted that the value obtained is a little bit lower than that equal to 2.2 and documented [4, 6]. Since the composition of electroplating solutions and electroplating conditions was the same, the difference in R_f might be assigned to differences in the real surface area of Pt substrates, which was electroplated by copper.

Electroless copper deposition from solutions containing L-, D- and DL-tartrate as Cu(II) ion ligands

It is documented that the stability constants of Cu(II) complexes with L- and DL-tartrate are very similar and a degree of Cu(II) ion complexation is practically the same [9]. Unfortunately, there are no data on interaction of Cu(II) with D-tartrate in alkaline solutions and, accordingly, Cu(II) complexation in alkaline D-tartrate solutions is not known. From the data available, the assumption can be stated that Cu(II) complex formation equilibria with D-tartrate might be very similar to that of Cu(II) and L-tartrate, Cu(II) ion complexation degree being the same. The light absorbance spectra of Cu(II) with different tartrate isomers confirms the above given assumption: the light absorption spectra of Cu(II) in alkaline solutions of L- and D-tartrate under the same conditions practically coincide (with the rare exceptions) (Fig. 1).

Despite the practically equal complexation level of Cu(II) in solutions of different isomers of tartaric acid, the para-

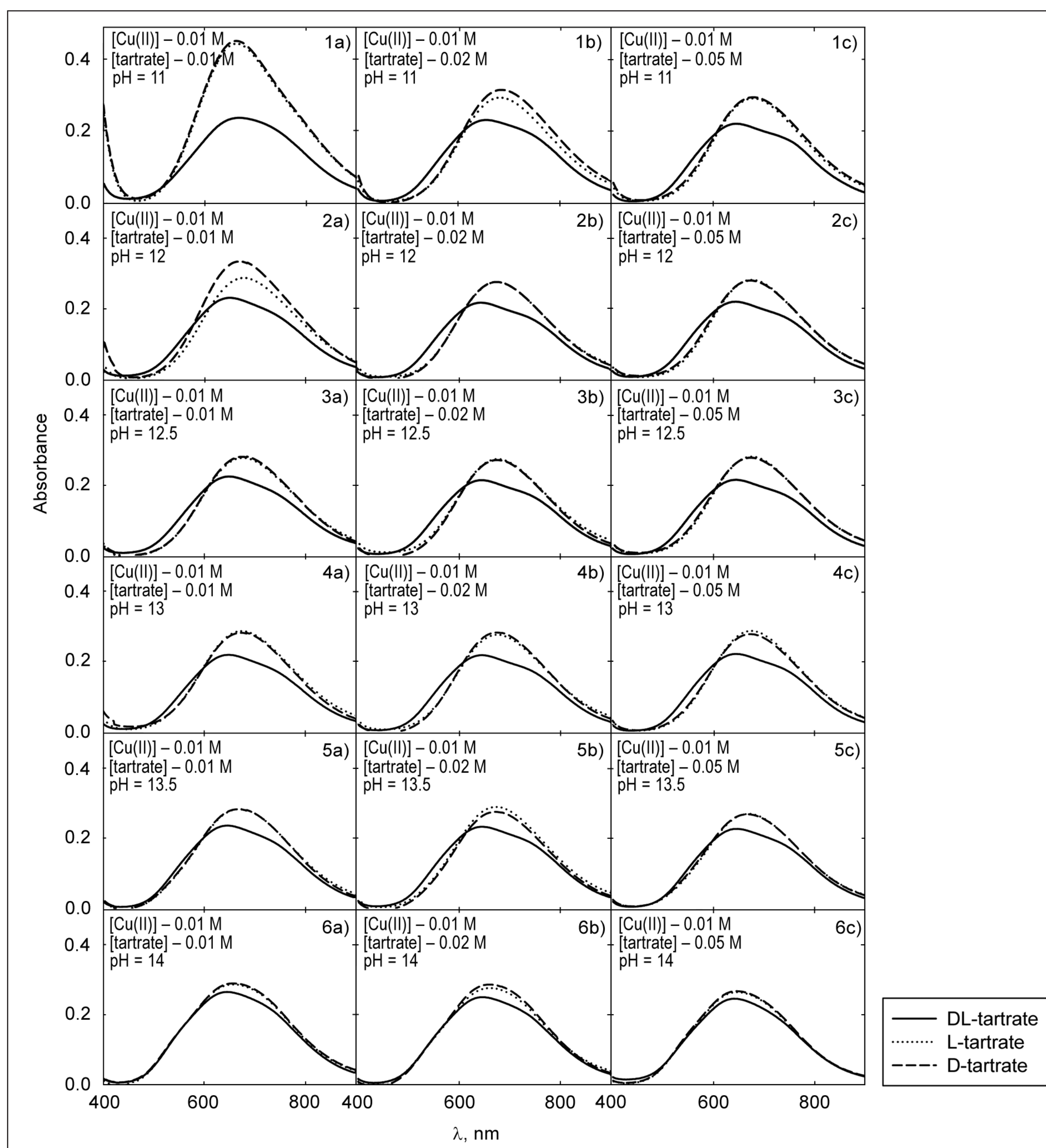


Fig. 1. Light absorbance spectra of Cu(II) in alkaline solutions of tartrate isomers

Table 1. Characteristics of the process of electroless copper deposition from D-, L- and DL-tartrate-containing solutions

t, °C	pH	*v*, μm h^{-1} after 30 min, after 60 min (redoubled)		R_f after 30 min, after 60 min		Most negative value of E_{mix}, mV	E_{mix}, mV after 25 min	E_{equil}, mV	Δ*E*, mV
Composition of electroless copper deposition solution (mol l^{-1}): [Cu(II)] – 0.05; [HCHO] – 0.15; [D-tartrate] – 0.15.									
10	12.0	0.7	0.7	5.6	6.0	–498	–353	–64	–289
	12.5	0.6	0.6	3.8	4.3	–587	–374	–98	–276
	13.0	0.8	0.5	2.5	2.5	–628	–374	–129	–245
20	12.0	0.9	0.8	4.2	4.6	–514	–345	–78	–267
	12.5	1.1	0.9	3.8	1.9	–622	–371	–114	–257
	13.0	1.2	0.9	3.1	1.6	–653	–366	–145	–220
30	12.0	1.4	1.6	4.4	4.4	–422	–304	–92	–211
	12.5	1.7	1.8	3.7	2.2	–567	–326	–129	–196
	13.0	2.0	2.0	2.3	2.5	–596	–325	–162	–163
Composition of electroless copper deposition solution (mol l^{-1}): [Cu(II)] – 0.05; [HCHO] – 0.15; [L-tartrate] – 0.15									
10	12.0	0.6	0.7	9.2	12.2	–512	–451	–64	–387
	12.5	0.4	0.6	6.1	6.0	–565	–456	–98	–357
	13.0	0.9	0.8	4.3	3.5	–606	–377	–129	–247
20	12.0	0.7	0.8	7.3	8.0	–491	–386	–78	–308
	12.5	1.2	1.0	3.7	4.4	–575	–428	–114	–314
	13.0	1.7	1.4	4.4	4.3	–616	–383	–145	–237
30	12.0	1.5	1.7	10.2	10.2	–489	–368	–92	–275
	12.5	2.0	1.7	5.4	5.6	–596	–343	–129	–213
	13.0	2.5	2.4	4.2	2.9	–594	–358	–162	–195
Composition of electroless copper deposition solution (mol l^{-1}): [Cu(II)] – 0.05; [HCHO] – 0.15; DL-tartrate] – 0.15									
10	12.0	1.0	1.0	7.9	9.2	–488	–309	–72	–237
	12.5	1.9	1.9	9.8	10.4	–568	–341	–108	–232
	13.0	0.9	0.8	5.4	6.1	–650	–371	–135	–236
20	12.0	1.8	1.7	6.2	5.9	–507	–296	–87	–208
	12.5	2.1	2.0	8.1	7.5	–596	–343	–124	–219
	13.0	1.6	1.4	4.7	4.4	–629	–345	–152	–192
30	12.0	2.9	2.9	5.0	5.5	–465	–269	–101	–167
	12.5	3.2	3.0	6.0	5.8	–575	–321	–140	–181
	13.0	2.5	2.4	4.0	3.1	–607	–340	–169	–171

meters of the process of electroless copper plating – copper plating rate, its dependence on pH and temperature, the real surface area of the copper coatings obtained differ measurably, especially in the case of DL-tartrate, comparing with individual isomers (Table 1 and Figs. 2–12).

In solutions containing an excess of the ligand (L-, D- or DL-tartrate), the autocatalytic reduction of Cu(II) by formaldehyde was investigated in pH region from 12 to 13, since at lower pH the reproducibility of the data obtained is unsatisfactory due to passivation of the copper surface, whereas the solutions with higher pH values contain sizeable amount of alkali and are unpractical.

The data obtained on electroless plating in solutions of different temperature (10, 20 and 30 °C) show the same trends after plating of both half hour and one hour duration (Fig. 2). The mass of deposited copper using L-tartrate or D-tartrate as copper(II) ligands practically coincide at lower pH (12.0 and 12.5), whereas at pH 13.0 the deposition of copper occurs more intensive using L-tartrate as a ligand of Cu(II) ions (Fig. 2). When using the racemic mixture of DL-tartrate, the distinct maximum is observed at pH 12.5 and the mass of deposited copper has the highest values from all isomers investigated. It can be noted that at pH 12.0 the use of DL-tartrate also causes the highest values of deposited copper, comparing with L-tartrate and D-tartrate.

The effect of temperature is as could be predicted, i. e. the increment of temperature results in higher values of the mass of the deposited copper. This is valid for all used isomers (Fig. 2).

The same tendencies are observed, when comparing the electroless copper plating rate, instead of the deposited copper mass (Fig. 3). It is worth noting that from the data of Fig. 3 it can be concluded that no surface passivation processes are observed in the systems under investigation: the comparison of the thickness of copper coating obtained after 30 min, which was recalculated to values corresponding to that after 1 hour, i. e. multiplied by two (the plating rate dimension being μm h^{-1}) (Fig. 3 1a, b and c), with that obtained after 1 hour plating (Fig. 3 2a, b and 2c) are very close to each other, showing no retardation processes taking part. It can be predicted from results obtained that the process of electroless copper deposition starts without a long induction period and quasi-stationary plating conditions are reached after a relatively short time at the pH values investigated.

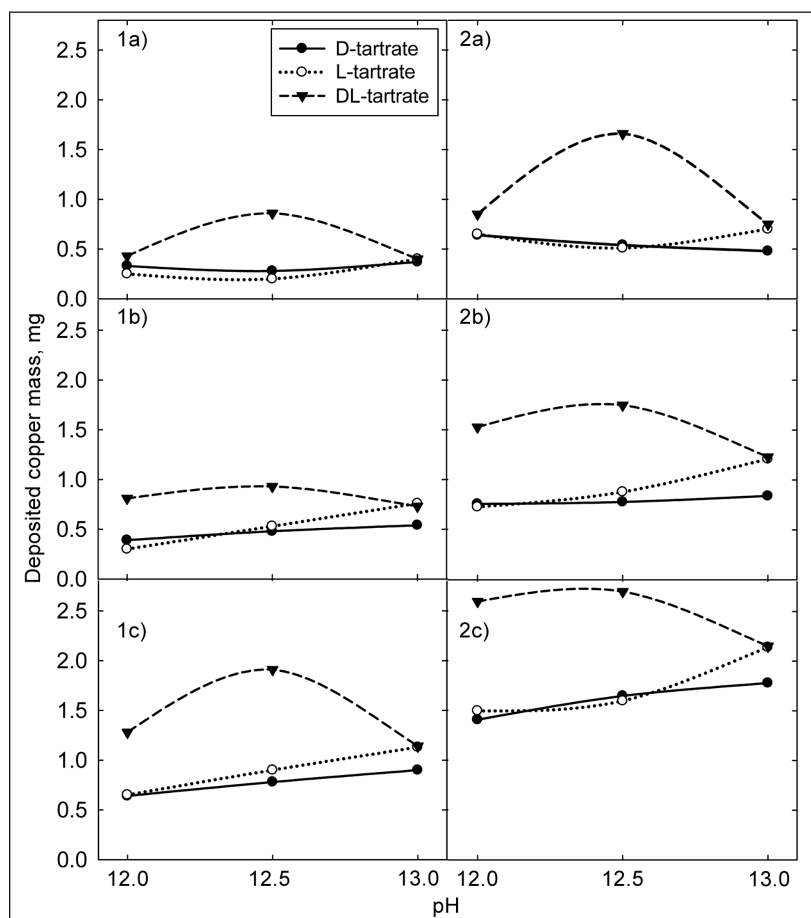


Fig. 2. Dependence of electrolessly deposited copper mass on pH and nature of ligand. Solution composition (mol l^{-1}): [Cu(II)] – 0.05, [HCHO] – 0.15, [tartrate] – 0.15. Temperature: a) 10 °C, b) 20 °C, c) 30 °C. Plating time: *1* – 0.5 h, *2* – 1 h

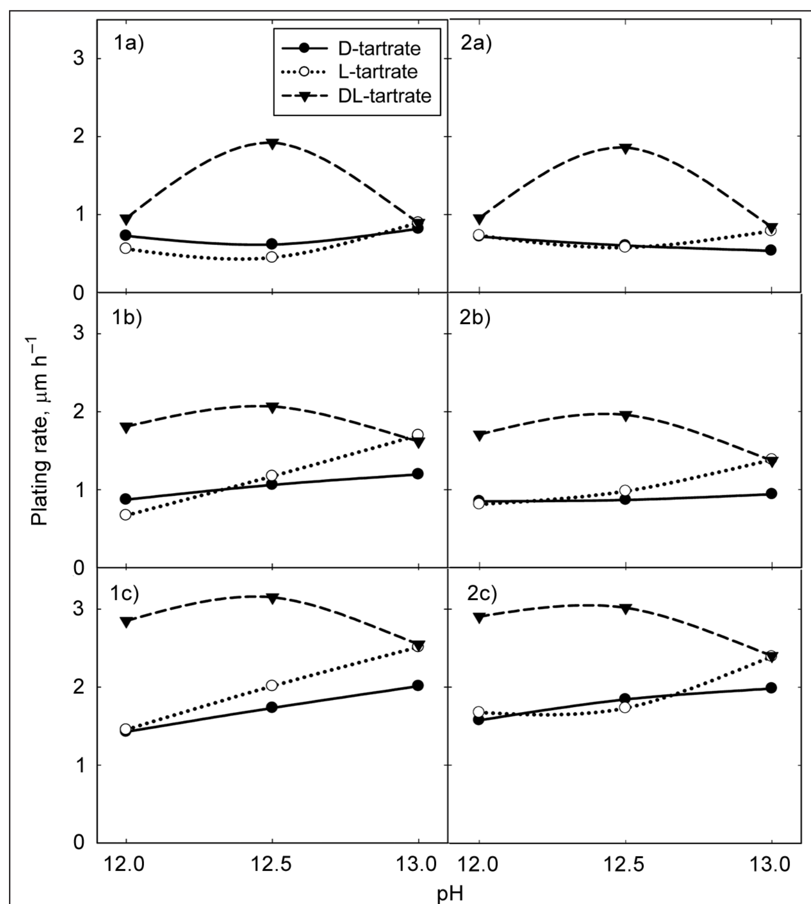


Fig. 3. Dependence of the copper plating rate on the pH and nature of the ligand. Solution composition (mol l^{-1}): [Cu(II)] – 0.05, [HCHO] – 0.15, [tartrate] – 0.15. Temperature: a) 10 °C, b) 20 °C, c) 30 °C. Plating time: *1* – 0.5 h, *2* – 1 h

The measurements of the mixed potential (E_{mix}), i. e. the potential of the copper electrode under open-circuit conditions, during electroless copper deposition process confirm the above-mentioned assumption (see below).

The pH dependencies of the plating rate at different temperatures were analyzed. In solutions with the lowest plating temperature (10 °C) and the lowest and highest investigated pH values (pH 12 and pH 13), the plating rates obtained are very close for all used isomers of tartaric acid (Fig. 3 1a and 2a) and do not exceed 1 μm h^{-1}. The comparable rates are observed for D-and L-tartrate also at pH 12.5, whereas in the case of the racemic mixture of DL-tartrate, the sharp increase in the plating rate is visible at pH 12.5 reaching ca. 2 μm h^{-1}. Rather similar trends are observed in electroless deposition of copper at higher temperatures (20 and 30 °C), except values obtained for L-and D-tartrate at pH 13, where the copper plating rate from L-tartrate containing solutions is apparently higher than that from D-tartrate solutions. The highest plating rate – ca. 3 μm h^{-1} – was obtained from the solutions containing the racemic mixture of DL-tartrate at pH 12.5 (Fig. 3 1c and 2c). The thickness of the compact copper coatings obtained under optimal operating conditions with different isomers in 1 h reaches from 0.5 to 3 μm (Table 1). It should be emphasized that the plating solutions are stable and no signs of Cu(II) reduction in the bulk solution were observed at least during one hour.

Roughness of electrolessly deposited copper coatings

Electrolessly deposited copper coatings in all cases have more developed surface than that of the electroplated copper (R_f = 1.5, see above), and the roughness factor varies in a wide range of values – from 1.6 to 12.2 depending on electroless copper plating solution pH, ligand used and temperature (Fig. 4 and Table 1).

It can be noted that, in general, the roughness of the coatings obtained after 0.5 hour is rather analogous to that obtained after 1 hour (Fig. 4). The results presented are in good agreement with the data on the measurements of the mixed potential of the copper electrode during the process of electroless copper plating (see below) – commonly the values of the mixed potential reach approximately constant values after ca. 15–20 min from the beginning of the process of electroless plating, and later plating occurs under the quasi-stationary conditions, the probability of substantial changes in the real surface area of the electrode being low. Additionally, it can be noted that electroless copper surface development occurs mostly in the first 15–30 min of the plating process, and later the surface area changes are insignificant [4].

Generally, the rise in temperature results in smoother coatings, i. e. with the surfaces of lower rougness factor (R_f) (Fig. 4).

pH-R_f dependencies for each used ligand differ. When using DL-tartrate as a Cu(II) ion ligand, the shape of pH-R_f

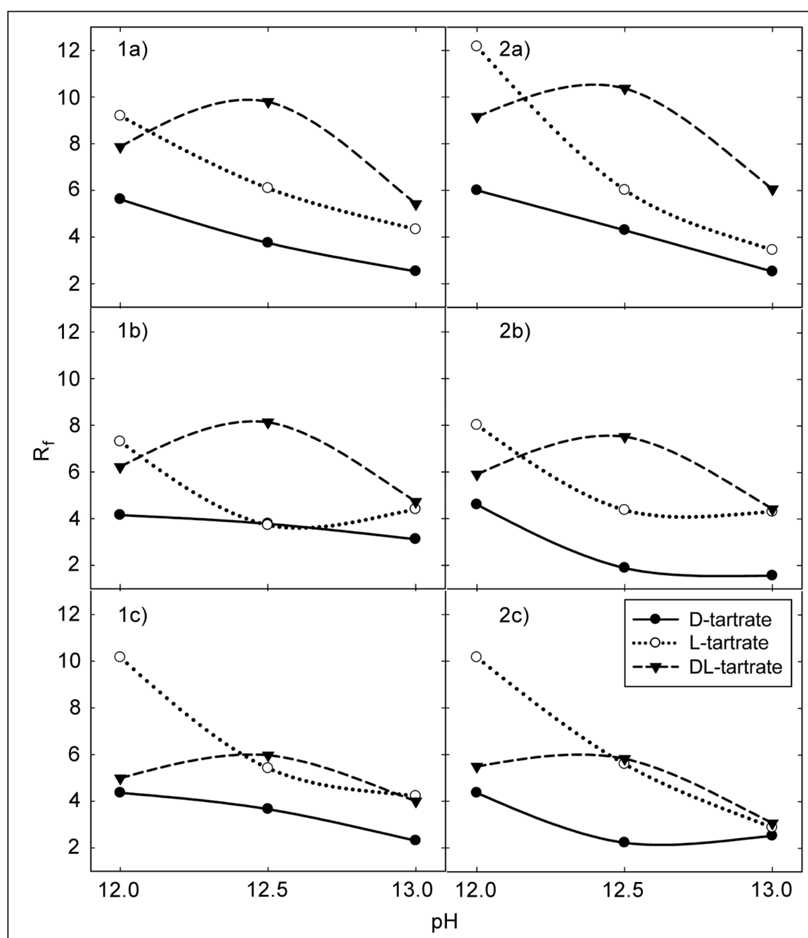


Fig. 4. Dependence of the copper surface roughness factor of electrolessly deposited copper coatings on the pH and nature of the ligand. Solution composition (mol l^{-1}): [Cu(II)] – 0.05, [HCHO] – 0.15, [tartrate] – 0.15; temperature: a) 10 °C, b) 20 °C, c) 30 °C. Plating time *1* – 0.5 h, *2* – 1 h

dependence (Fig. 4) remind that of pH-plating rate (Fig. 3), i. e. with the distinct maximum at pH 12.5. In the case of L- or D-tartrate, the shape of pH-R_f dependence (Fig. 4) is opposite than that of pH-plating rate dependence – the highest values of R_f are observed at lower pH limit investigated, and the increase in solution pH results in decrease of R_f. In all cases at the same solution pH and different used ligands, the smoothest coatings were observed when using D-tartrate as a Cu(II) ligand.

The smoothest copper coating was deposited from D-tartrate solutions at pH 13 (20 °C) – R_f = 1.6 was very close to that of the electroplated copper (R_f = 1.5). The highest R_f values were obtained for copper coatings deposited from L-tartrate solution at pH 12 and 10 °C (R_f = 12.2), and from DL-tartrate solution at pH 12.5 and the same temperature (R_f = 10.4).

The open-circuit potential of copper electrode during electroless deposition

The open-circuit potential of copper in the course of electroless deposition at pH 12–13 varies over a rather wide range of values depending on the solution pH, tartrate isomer used and temperature (Figs. 5 and 6). As the process of autocatalytic copper(II) reduction (electroless metal deposition) is generally accepted to be electrochemical by nature (the electrons appearing in formaldehyde anodic oxidation are transferred through metallic copper to copper(II) ions), the open-circuit potential in this case is a mixed one (E_{mix}). The potential is established as a result of two reactions occurring simultaneously on the same copper surface – cathodic reduction of Cu(II) ions and anodic oxidation of formaldehyde. The time-dependence curves of E_{mix} are typical for alkaline formaldehyde-containing electroless copper plating solutions [5, 10]. With the aim of more detailed analysis of the data obtained, the time dependencies of the mixed potential (E_{mix}) of the copper electrode during the electroless copper plating process are presented in two manners: 1) time dependencies of E_{mix} of the copper electrode at corresponding temperatures in solutions of the same tartrate isomer at different solution pH values (Fig. 5), and 2) time dependencies of E_{mix} of the copper electrode at corresponding temperatures in solutions with the same pH value and different tartrate isomers (Fig. 6).

During the initial period after immersion of the activated electrode into the electroless copper plating solution (i. e. from the first seconds and up to 2 minutes), E_{mix} reaches its most negative value, later shifting to more positive potentials. After ca. 15 minutes it remains practically constant (or shifts negligible to more positive potentials) due to the establishment of quasi-stationary plating conditions (Figs. 5 and 6). It can be noted that the initial period is the largest for electroless copper plating solutions working at the lowest investi-

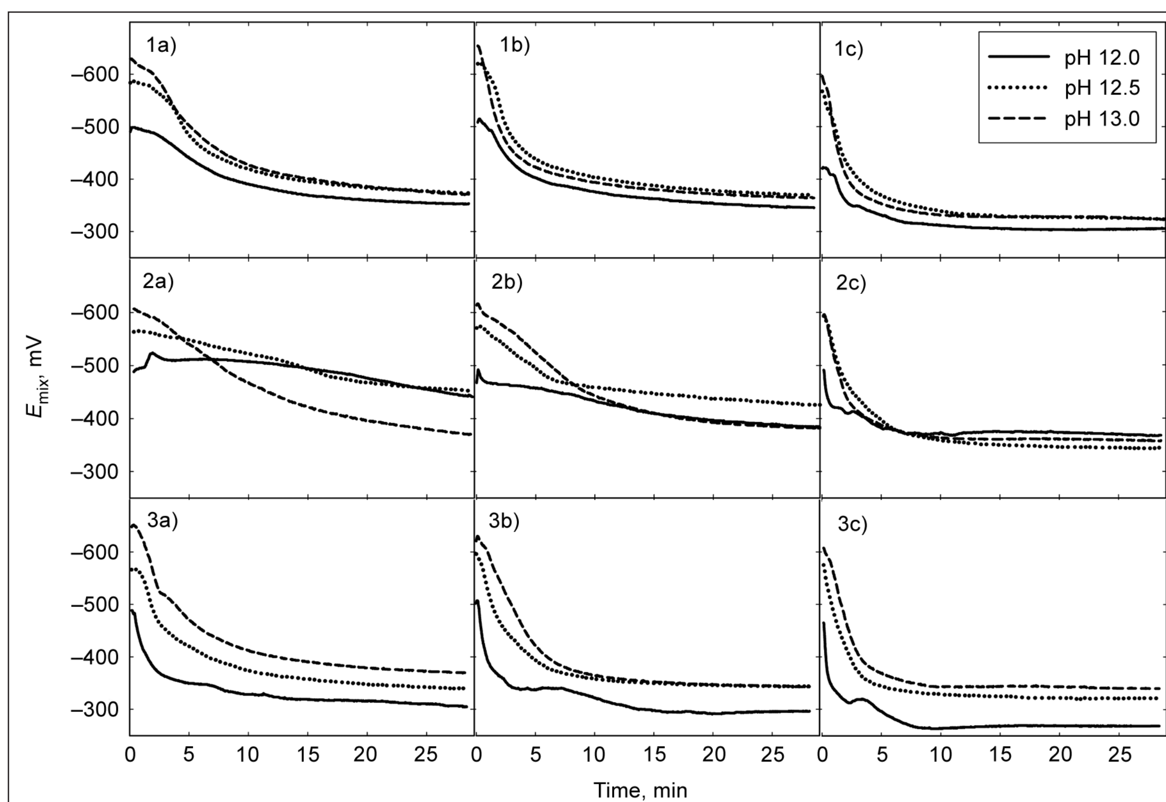


Fig. 5. Time dependence of the mixed potential (E_m) of the copper electrode during electroless copper plating. Solution composition (mol l^{-1}): [Cu(II)] – 0.05, [HCHO] – 0.15, [tartrate] – 0.15: 1) D-tartrate, 2) L-tartrate, 3) DL-tartrate. Copper deposition temperature: a) 10 °C, b) 20 °C, c) 30 °C

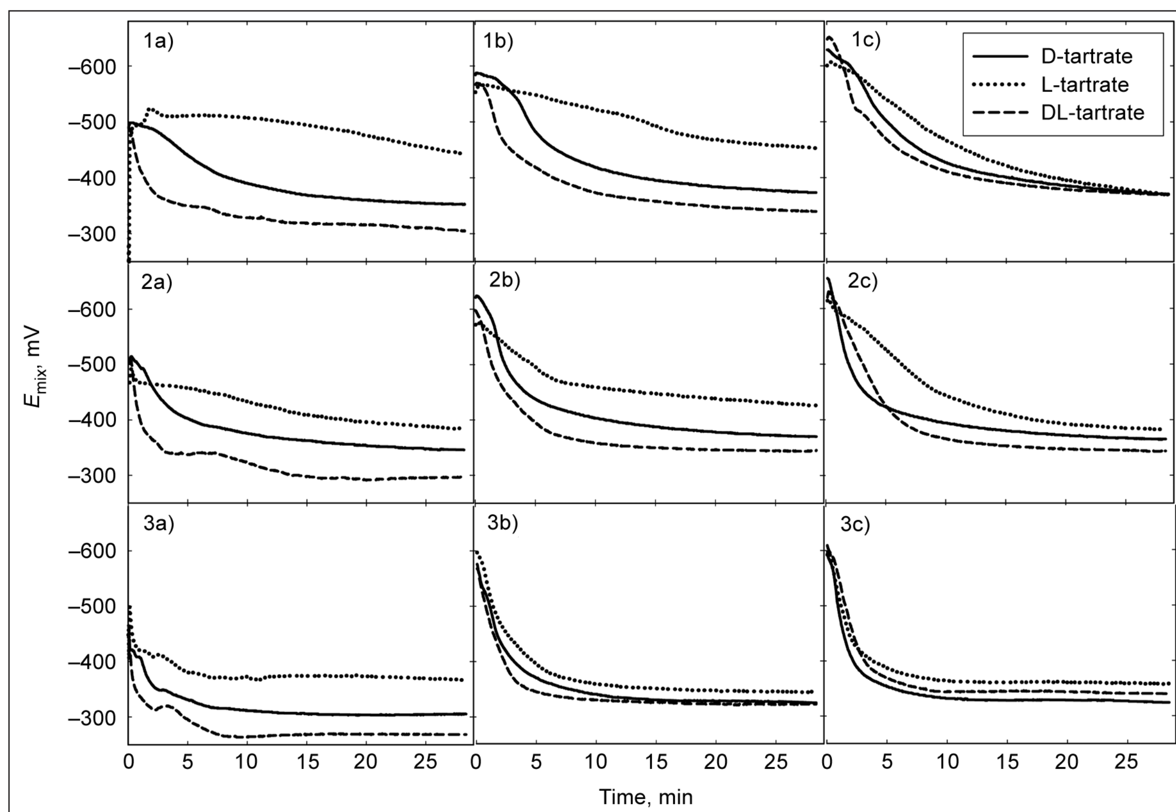


Fig. 6. Time dependence of the mixed potential (E_{mix}) of the copper electrode during electroless copper plating. Solution composition (mol l^{-1}): [Cu(II)] – 0.05, [HCHO] – 0.15, [tartrate] – 0.15. Copper deposition temperature: 1) 10 °C, 2) 20 °C, 3) 30 °C; pH: a) 12.0, b) 12.5, c) 13.0

gated temperature (10 °C), reaching 2 min (Fig. 5 1a–c and Fig. 6 1a–3a), comparing with that obtained at 20 and 30 °C.

After establishing of quasi-stationary conditions, in most presented cases, the mixed potential shifts continuously to more negative values with the rise in solution pH (Fig. 5), corresponding to the shift of the potential regions in both the electrochemical half-reactions of the catalytic process. One difference from the most other investigated electroless copper plating systems using different ligands is observed – the difference between the most positive and the most negative values of E_{mix} in Cu(II)-tartrate-formaldehyde system is quite small (like in Cu(II)-citrate-formaldehyde system [3]) and does not exceed ca. 90 mV when pH changes from 12 to 13 (Fig. 5), whereas in other systems this difference can reach ca. 200 [11] or even 300 mV [12].

It is also seen that the temperature increment, in general, results in the modest shift of the E_{mix} to the side of more positive potentials (Figs. 5 and 6). Much more distinct effects of the nature of the ligand were observed measuring time dependencies of E_{mix} at similar conditions, but using different tartrate isomer as a Cu(II) ligand (Fig. 6). The following general trend was found (particulary expressed in solutions with pH 12 (Fig. 6 1a–3a)) – the most negative values of E_{mix} are characteristic of L-tartrate solutions, the values of E_{mix} in D-tartrate solutions are more positive (comparing with L-tartrate), and in solutions of DL-tartrate E_{mix} has the most positive values. This difference between the most negative and the most positive values, depending on pH, can reach 100 or more mV (Fig. 6).

A clear correlation between the plating rate and values of E_{mix} (Fig. 6) is observed – the highest plating rates under the similar conditions were determined in DL-tartrate containing solutions (Fig. 3), which exhibit the most positive E_{mix} values (Fig. 6), whereas the lowest plating rates were estimated in D-tartrate containing solutions. The highest numerical value of the electroless copper deposition rate obtained – 3.2 μm h^{-1} – was achieved in DL-tartrate solutions with pH = 12.5 at 30 °C, the E_{mix} numerical value being –321 mV, i. e. corresponding to one of the most positive values measured (Figs. 3, 6 and Table 1). In opposite, the lowest numerical value of the electroless copper deposition rate obtained – 0.4 μm h^{-1} – was measured in L-tartrate solutions with pH = 12.5 at 10 °C, the E_{mix} numerical value being –456 mV, i. e. corresponding to the most negative value measured in our experiments (Figs. 3, 6 and Table 1). The data obtained are in good agreement with the earlier documented relationship that more positive E_{mix} values correspond, as the rule, to higher plating rates [7, 13].

The overpotential (Δ*E*) of copper electrode in alkaline solutions of tartate isomers

The electrode overpotential in the systems of electroless metal deposition is defined as the difference between the mixed

potential (E_{mix}) and equilibrium potential (E_{equil}) of metal electrode: $\Delta E = E_{mix} - E_{equil}$. In our case, the values of the mixed potential were taken after 25 min from the beginning of electroless copper deposition process (Table 1), whereas the values of the equilibrium potential of a Cu/Cu^{2+} electrode (E_{equil}) were calculated according to the Nernst equation using the data on the mass balance and the stability constants of the Cu(II) complexes existing in the solutions (taken from Ref. 9, additionally assuming that Cu(II) complex formation equilibria with D-tartrate might be very similar to that of Cu(II) and L-tartrate, Cu(II) ion complexation degree being the same). Figure 7 shows the dependencies of the overpotential of the copper electrode on the solution pH. When comparing the overpotential values obtained, it is seen that the overpotential is the most negative for L-tartrate containing solutions and the most positive for DL-tartrate containing solutions, the values of ΔE in D-tartrate solutions being between the mentioned two values. It can be noted that the largest difference between ΔE values of L-tartrate and DL-tartrate containing electroless plating solutions was observed at pH 12, whereas this difference was the smallest at pH 13 (Fig. 7). It was found that, generally, the increment in temperature (from 10 to 30 °C) results in the shift of the overpotential to more positive values (Fig. 7). The comparison of the overpotential values with other parameters of the electroless copper plating systems with different isomers of tartaric acid is described herein after.

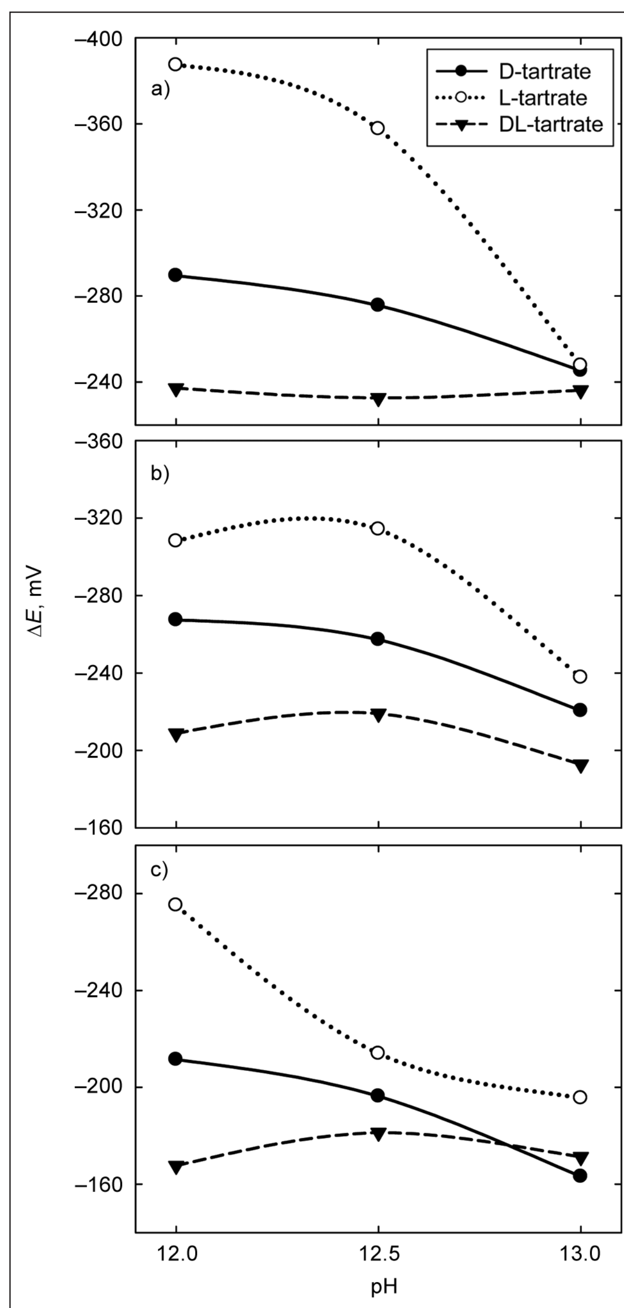
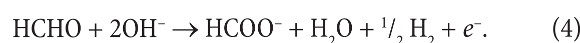


Fig. 7. Dependence of the overpotential (ΔE) of the copper electrode on pH. Solution composition (mol l^{-1}): [Cu(II)] – 0.05, [HCHO] – 0.15, [tartrate] – 0.15. Copper deposition temperature: a) 10 °C, b) 20 °C, c) 30 °C

Voltammograms of copper electrode in alkaline solutions of formaldehyde and formaldehyde oxidation rates

Voltammograms were recorded using four different types of copper electrodes. The surface of the first electrode was formed by electroplating from an acidic copper(II) sulphate electrolyte. The other three types were prepared by electroless copper plating technique (at 10, 20 and 30 °C) from solutions containing D-tartrate, L-tartrate and DL-tartrate, respectively, as Cu(II) ligand at pH values corresponding to those of the solutions under electrochemical investigations.

Fig. 8 presents voltammograms of the electroplated copper electrode in alkaline solutions of formaldehyde. At the positive-going potential scan anodic current is observed over the potential interval ca. 0.6 V; this current is known to be a result of anodic formaldehyde oxidation according to the equation (4), since in the absence of formaldehyde no current is observed in this potential region:



$$HCHO + 2OH^- \rightarrow HCOO^- + H_2O + {}^1/_2\, H_2 + e^-. \qquad (4)$$

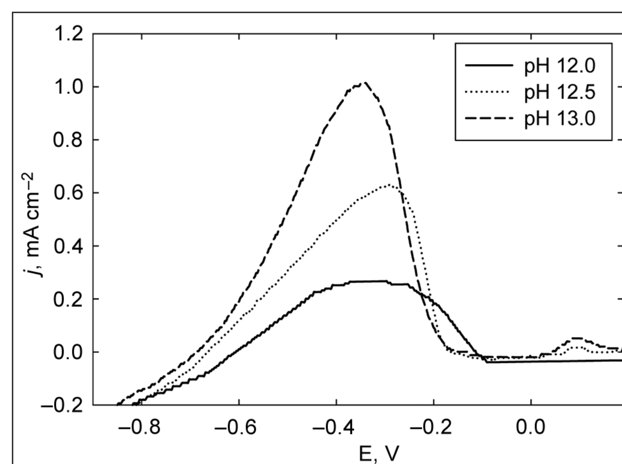


Fig. 8. Voltammograms of the copper electrode (formed by electroplating) in alkaline solutions of formaldehyde. Solution composition (mol l^{-1}): [Na_2SO_4] – 0.1; [HCHO] – 0.15. Solution temperature – 20 °C

The anodic current drops abruptly at potentials around −0.25 – −0.15 V in the result of copper surface oxidation with the formation of Cu_2O (or chemisorbed oxygen) monolayer which inhibits HCHO oxidation. The potential of anodic current fall (surface passivation) shifts to more negative values with a rise of solution pH from 12 to 13, as could be expected for the Cu/Cu_2O couple. Later, at the potentials more positive than 0.0 V, the distinct anodic current is observed only at higher solutions pH, i. e. 12.5 and 13.0 (Fig. 8). The mentioned current corresponds to more deep Cu oxidation with formation of Cu(II) oxy-and hydroxy-compounds [6]. In solutions with pH 12.5 and 13.0, the current of formaldehyde anodic oxidation rises with the potential (positive potential scan), and the maximal current values are obtained immediately before the current fall due to the oxidation of the copper electrode surface (Fig. 8 and Table 3). The voltammogram obtained in solutions with pH 12.0 differs from the above mentioned – in a comparatively wide potential interval (approximately from −0.5 V to −0.2 V) the current changes only marginally. This potential interval of formaldehyde oxidation is more wide compared with voltammograms obtained at higher pH values, due to the more positive value of Cu surface oxidation. A more detailed explanation of this phenomenon based on pH decrease at the electrode surface is given in literature [6].

The shape and the values of the formaldehyde anodic oxidation current differ significantly, when comparing such data obtained on the electroplated copper electrode with that measured on electrolessly deposited copper coatings (cf. Fig. 8 and Fig. 9). In general case, the values of the anodic oxidation of formaldehyde on electrolessly deposited copper surfaces are much higher (in some cases more than five times) than those obtained on the electroplated copper electrode (cf. Figs. 8 and 9 and Tables 2 and 3).

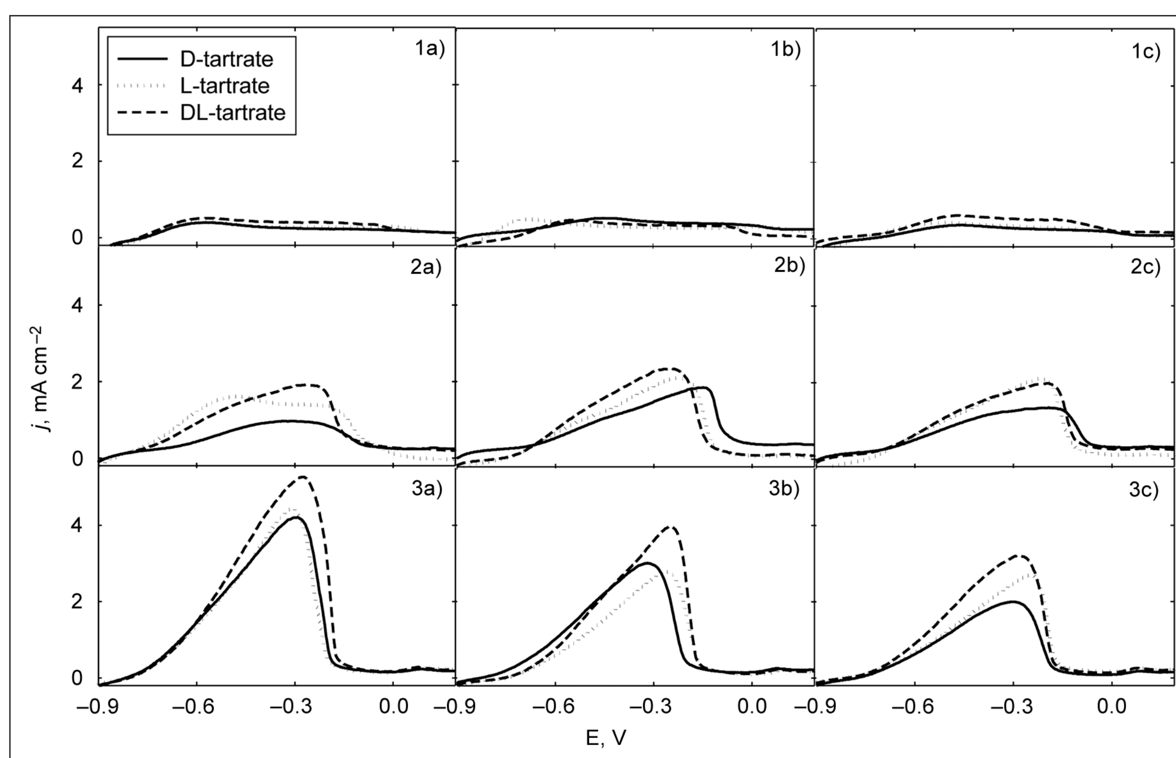


Fig. 9. Voltammograms of the copper electrode in alkaline solutions of formaldehyde. Solution composition (mol l^{-1}): [Na_2SO_4] – 0.1; [HCHO] – 0.15. Solution temperature – 20 °C. Electrode surface was formed by electroless plating from tartrate isomers containing solutions. Plating solution composition (mol l^{-1}): [Cu(II)] – 0.05, [HCHO] – 0.15, [tartrate] – 0.15. Plating conditions: pH – 1) 12.0, 2) 12.5, 3) 13.0; temperature – a) 10 °C, b) 20 °C, c) 30 °C

Table 2. **Parameters of the anodic oxidation of CH_2O in alkaline solutions on the copper electrode formed by electroplating. Solution composition (mol l^{-1}): [HCHO] – 0.15; [Na_2SO_4] – 0.1. 20 °C (S_G = 1 cm^2, S_{R0} = 1.5 cm^2, R_{f0} = 1.5)**

pH	E_p, mV	j_{pG} (current peak density corresponding to the geometrical surface area), mA cm^{-2}	j_{pR} (current peak density corresponding to the real surface area), mA cm^{-2}
12.0	−293	0.26	0.17
12.5	−289	0.62	0.41
13.0	−348	1.01	0.67

The anodic oxidation of formaldehyde is sensitive to the Cu surface structure: the process study on single-crystal electrodes showed the plane Cu(110) to be considerably more active compared with the planes Cu(100) and Cu(111) [15]. The rate of formaldehyde oxidation on polycrystalline copper surfaces may depend on surface formation conditions, e. g. it was found to be different on Cu coatings deposited from electroless plating solutions containing various Cu(II) ligands [13]. The correlation between the changes in the electroless copper plating rate and the copper surface nano-scale roughness was found in some cases, and this correlation should be expected to exist due to the formaldehyde anodic oxidation rate dependence on the Cu surface area [4].

When analyzing the data of Table 3 and Fig. 9, no big differences are observed in anodic oxidation curves of formaldehyde at pH 12.0, i. e. all copper coatings electrolessly deposited from solutions containing D-, L- and DL-tartrate as Cu(II) ligands at 10, 20 and 30 °C exhibit similar properties, the maximum anodic oxidation current density values being from 0.36 to 0.61 mA cm^{-2} (Table 3), the lowest value obtained for L-tartrate (plating at 30 °C), and the highest value for DL-tartrate (plating at 30 °C). In all cases in solutions with higher pH value and equal to 12.5, the current densities have 3–4 times higher values than those obtained at pH = 12.0 (Table 3 and Fig. 9). At pH = 12.5, the highest formaldehyde anodic oxidation peak current density values were measured on copper electrodes coated with electroless copper at 20 °C in solutions of all three isomers. When comparing the copper coatings deposited from solutions of different isomers at the same temperature (10, 20 or 30 °C), it can be noted that the currents of formaldehyde anodic oxidation (at pH 12.5) mainly are the highest in the case of DL-tartrate, and the lowest for D-tartrate (Fig. 9 and Table 3). The same general trend is evident during the oxidation of formaldehyde at pH 13 (Fig. 9 and Table 3). An additional interesting and clear seen peculiarity was unrolled at the mentioned pH value – for all three above mentioned kinds of electrolessly deposited copper coatings the highest formaldehyde oxidation rates were obtained for coatings, deposited at the lowest, i. e. 10 °C, temperature, whereas the coatings deposited at 30 °C are at the least active in anodic oxidation of formaldehyde (Fig. 9 and Table 3).

Specific activity of Cu surfaces in formaldehyde anodic oxidation reaction

The specific activity of the copper surface (formaldehyde anodic oxidation peak current per unit of real surface area) was calculated from the data in Fig. 9 for comparing the electrocatalytic properties of various copper layers obtained by electroless plating technique using different isomers of tartaric acid as Cu(II) ligands (Table 3, also Table 2 for electroplated copper electrode).

According to the results obtained, the specific activity data can be divided into two groups: 1) those for formaldehyde oxidation at pH 12.0, and 2) for oxidation at pH 12.5–13.0.

The specific activity of various copper surfaces at pH 12.0 ranges from 0.04 to 0.13 mA cm^{-2}, but the most activity values are in the smaller interval of 0.04–0.08 mA cm^{-2} (Table 3 and Figs. 10–12). It is worth noting that at pH 12.0 the specific activity of all electrolessly deposited coatings are lower than that of the electroplated copper, i. e. 0.17 mA cm^{-2} (Table 2).

The specific activity of Cu surfaces in formaldehyde solutions at pH 12.5 and 13.0 (Table 3 and Figs. 10–12) also varies in a large range of values – from 0.19 to 1.66 mA cm^{-2}. At solution pH 13.0, the values of specific activity in all cases are higher than those at pH 12.5 and vary from 0.64 to 1.66 mA cm^{-2} (0.67 mA cm^{-2} for electroplated copper), whereas the values of specific activity of copper surfaces in solutions with pH 12.5 are in the range from 0.19 to 0.58 mA cm^{-2} (0.41 mA cm^{-2} for electroplated copper) (Tables 2 and 3).

Table 3. **Parameters of the anodic oxidation of CH_2O in alkaline solutions on the electrolessly formed copper electrode. Solution composition (mol l^{-1}): [HCHO] – 0.15; [Na_2SO_4] – 0.1. 20 °C**

Temperature of coating deposition	10 °C			20 °C			30 °C		
pH	E_p, mV	j_{pG}, j_{pR} mA cm^{-2}		E_p, mV	j_{pG}, j_{pR} mA cm^{-2}		E_p, mV	j_{pG}, j_{pR} mA cm^{-2}	
Electroless plating solution (mol l^{-1}): [Cu(II)] – 0.05; [HCHO] – 0.15; [D-tartrate] – 0.15. Plating time – 0.5 h									
12.0	–610	0.39	0.07	–426	0.54	0.13	–454	0.36	0.08
12.5	–357	0.96	0.26	–151	1.87	0.50	–203	1.33	0.36
13.0	–299	4.20	1.66	–315	3.00	0.96	–296	1.99	0.86
Electroless plating solution (mol l^{-1}): [Cu(II)] – 0.05; [HCHO] – 0.15; [L-tartrate] – 0.15. Plating time – 0.5 h									
12.0	–600	0.41	0.04	–687	0.51	0.07	–520	0.43	0.04
12.5	–470	1.61	0.26	–236	2.11	0.58	–237	2.09	0.38
13.0	–275	4.44	1.02	–257	2.77	0.63	–248	2.69	0.64
Electroless plating solution (mol l^{-1}): [Cu(II)] – 0.05; [HCHO] – 0.15; [DL-tartrate] – 0.15. Plating time – 0.5 h									
12.0	–601	0.51	0.06	–553	0.48	0.08	–478	0.61	0.12
12.5	–280	1.91	0.19	–242	2.35	0.29	–194	1.97	0.33
13.0	–263	5.26	0.97	–249	3.96	0.83	–282	3.20	0.80

It can be noted that in all investigated cases the shape of the formaldehyde anodic oxidation peak current dependence on the solution pH for currents obtained for the geometrical surface area is very similar to that calculated for the real surface area (Figs. 10–12d, e).

Generalization of the obtained results

The data presented in Figs. 10–12 allow to see the general picture and compare the pH dependencies of different parameters of the electroless deposition process using D-, L- and DL-tartrate as a copper(II) ligand, namely, the copper plating rate (a), overpotential of the copper electrode (b), copper surface roughness factor (c), HCHO anodic oxidation current peak density (corresponding to the geometrical surface area) (d), HCHO anodic oxidation current peak density (corresponding to the real surface area) (e).

First, the data obtained at 20°, where all experiments including electrochemical measurements were carried out at the same mentioned temperature, are analysed. In the case of D-tartrate, a clear directly proportional correlation between the plating rate and the formaldehyde anodic oxidation peak current is observed (cf. Fig. 10 1a, d, e), while the overpotential of the copper electrode (ΔE) and the surface roughnes (R_f) are inversely proportional to the electroless copper

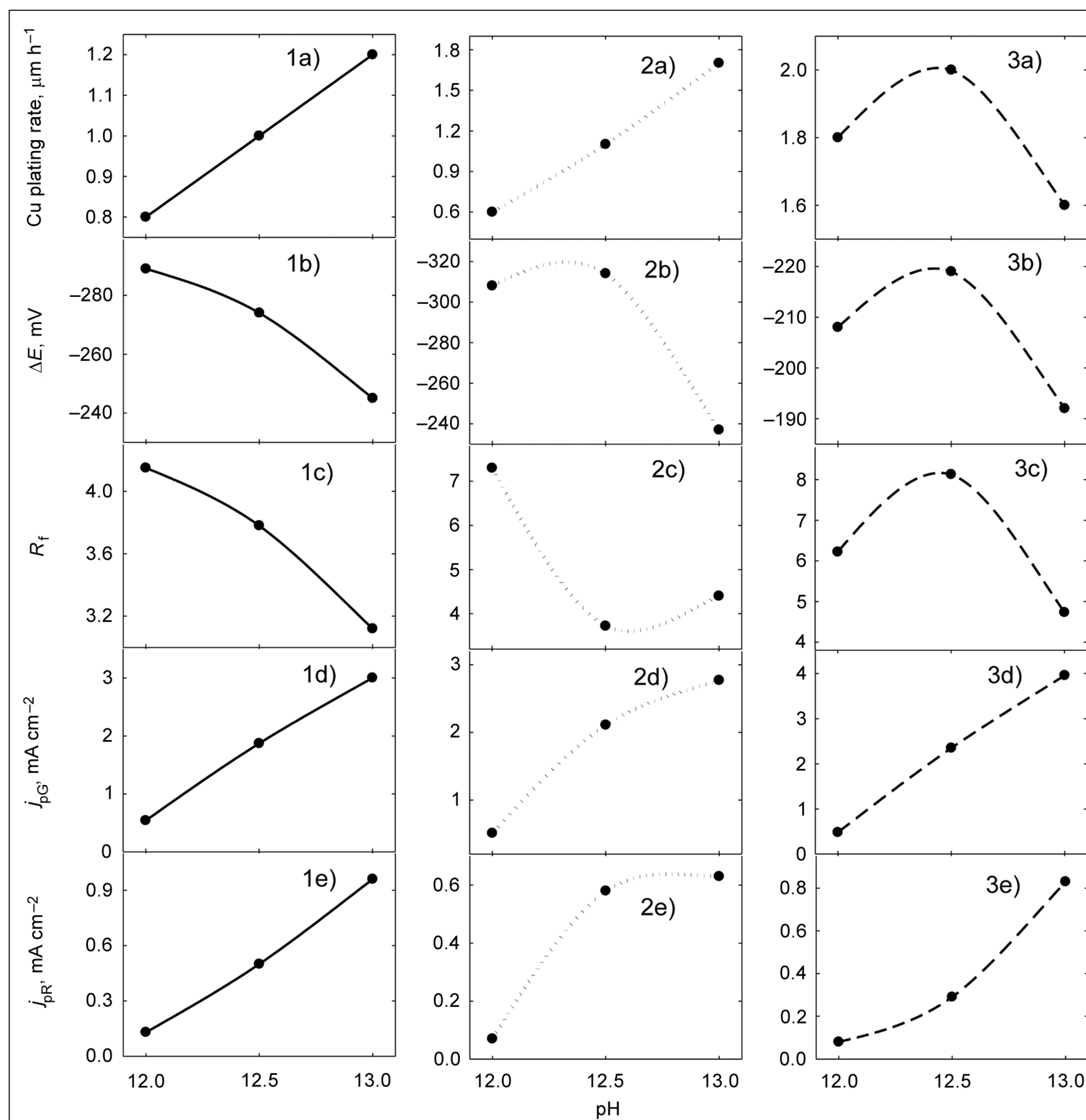


Fig. 10. Dependence of the copper plating rate (a), overpotential of the copper electrode (b), copper surface roughness factor (c), HCHO anodic oxidation current peak density (corresponding to the geometrical surface area) (d), HCHO anodic oxidation current peak density (corresponding to the real surface area) (e) on pH. Solution composition (mol l^{-1}): [Cu(II)] – 0.05, [HCHO] – 0.15, [tartrate] – 0.15: 1) D-tartrate, 2) L-tartrate, 3) DL-tartrate. Temperature of solutions: a)–e) – 20 °C

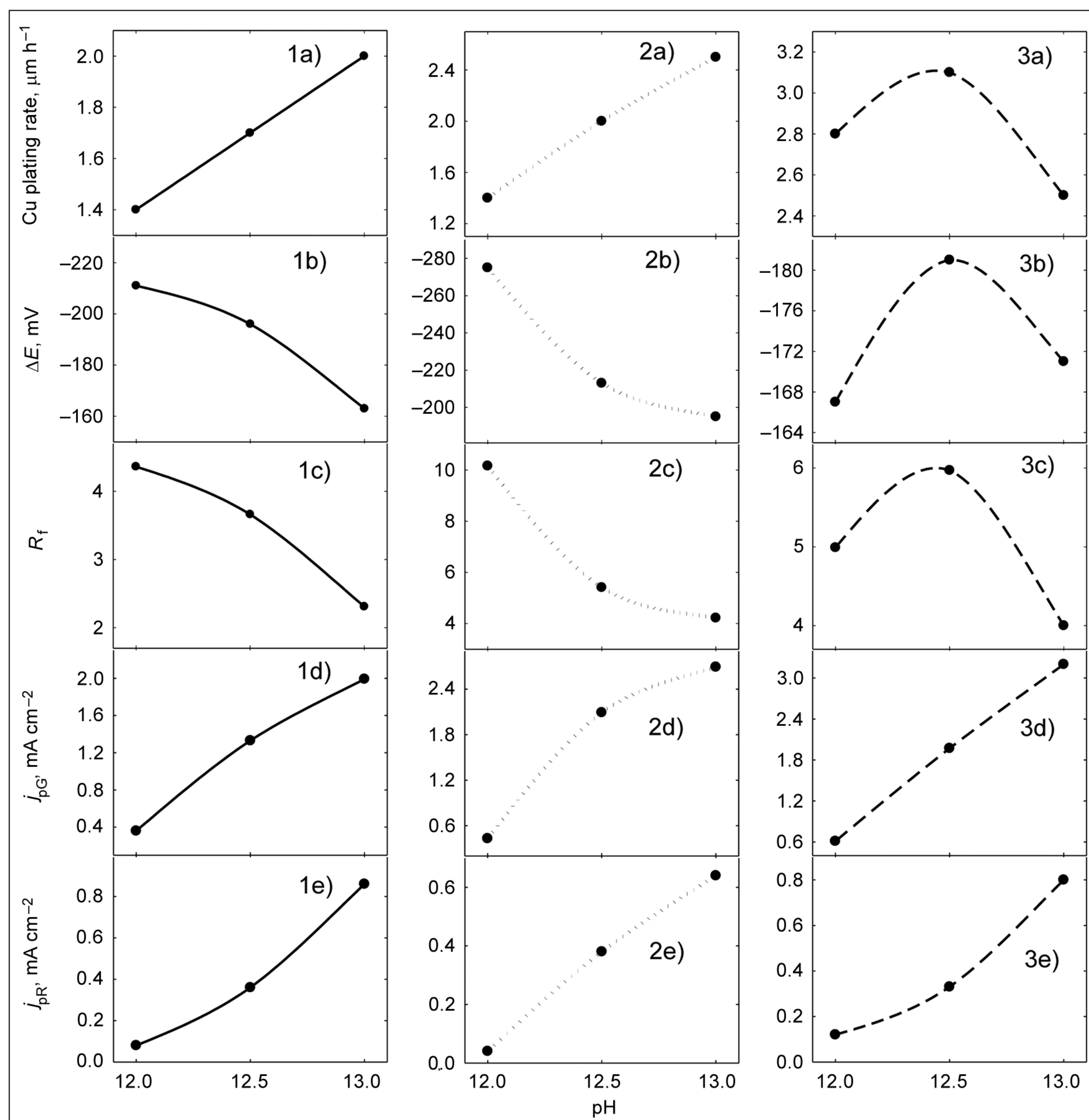


Fig. 11. Dependence of the copper plating rate (a), overpotential of the copper electrode (b), copper surface roughness factor (c), HCHO anodic oxidation current peak density (corresponding to the geometrical surface area) (d), HCHO anodic oxidation current peak density (corresponding to the real surface area) (e) on pH. Solution composition (mol l^{-1}): [Cu(II)] – 0.05, [HCHO] – 0.15, [tartrate] – 0.15: 1) D-tartrate, 2) L-tartrate, 3) DL-tartrate. Temperature of solutions: a)–c) – 30 °C; d) and e) – 20 °C

plating rate (cf. Fig. 10 1a, b, c). The comparable results are observed for L-tartrate (Fig. 10 2a, e), except ΔE and R_f dependencies, where extreme values are observed at pH 12.5 (Fig. 10 2b, c). When using DL-tartrate as a copper(II) ligand, a similar shape is seen for pH dependencies of the electroless copper deposition rate, ΔE and R_f – in all cases the extremum value was determined at pH 12.5 (Fig. 10 3a, c), whereas the anodic oxidation peak current density of formaldehyde rises with increase in solution pH (Fig. 10 3d, e).

A very similar picture is observed when comparing results of investigations carried out at the elevated temperature, i. e. at 30 °C (Fig. 11), with those conducted at 20 °C (Fig. 10). It can be noted that the trends are practically the same for D-tartrate, L-tartrate and DL-tartrate containing solutions, the differences are only in numerical values of parameters.

Again, when temperature of electroless copper deposition experiments was lowered to 10 °C (Fig. 12), the shape of the investigated dependencies in most cases corresponds to that obtained in solutions of 20 °C (Fig. 10), except some differences in pH dependencies of the plating rate for D-tartrate and L-tartrate (cf. Fig. 12 1a and 2a with Fig. 10 1a and 2a), having minimum values at pH 12.5. The data on ΔE in DL-tartrate solutions also differ for both temperatures – at 10 °C the overpotential (ΔE) remains practically independent

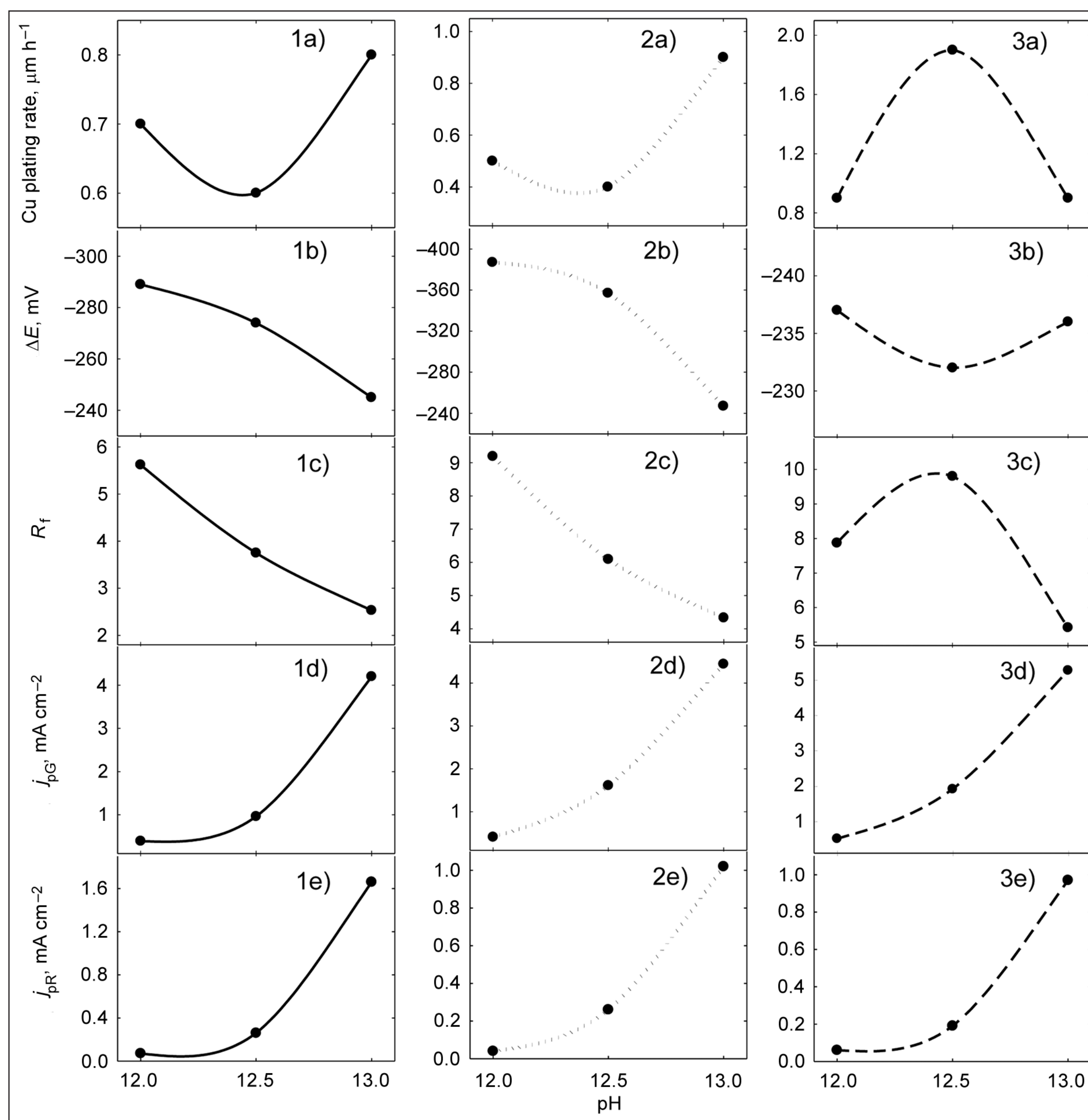


Fig. 12. Dependence of the copper plating rate (a), overpotential of the copper electrode (b), copper surface roughness factor (c), HCHO anodic oxidation current peak density (corresponding to the geometrical surface area) (d), HCHO anodic oxidation current peak density (corresponding to the real surface area) (e) on pH. Solution composition (mol l^{-1}): [Cu(II)] – 0.05, [HCHO] – 0.15, [tartrate] – 0.15: 1) D-tartrate, 2) L-tartrate, 3) DL-tartrate. Temperature of solutions: a)–c) – 10 °C; d) and e) – 20 °C

on solution pH (with inconsiderable minimum at pH 12.5) (Fig. 12 3b), whereas at 20 °C it has well-expressed maximum at the same pH (Fig. 12 3b).

Comparison of tartrates containing electroless plating systems with the systems operating with other copper ligands

Primarily, it should be noted that electroless copper plating experiments with D-tartrate as a copper(II) ligand were conducted for the first time, no literature data have been found. The experimental data on electroless copper plating using tartrates as copper(II) ligands at diminished (10 °C) or elevated (30 °C) temperatures, according to our literature search, are also absent.

With the aim to compare our data with those obtained with the same or other copper(II) ligands, we have selected literature data for electroless copper plating process parameters collected under similar experimental conditions using different ligands (20 °C temperature, 1 hour plating time, concentrations of copper(II) salt and formaldehyde equal to 0.05 mol l^{-1} and 0.15 mol l^{-1}, respectively).

The rate of copper deposition in tartrates-containing electroless copper solutions under optimal operating conditions reaches about 2.0 μm h^{-1} (pH 12.5) for DL-tartrate, 1.4 μm h^{-1}

(pH 13.0) for L-tartrate and 0.9 μm h^{-1} (pH 12.5–13.0) for D-tartrate (Fig. 3, Table 1). Similar or slightly higher rates (2–2.5 μm h^{-1}) were determined using other environment-friendly compounds such as citric acid (3 μm h^{-1} at pH 12.75) [3], saccharose (2 μm h^{-1} at pH 12.75) [11], xylitol, D-mannitol and D-sorbitol as Cu(II) ligands, but for three last ligands the required pH values were much higher and reached 13.5–13.8 [16]. Plating rates that where higher were obtained from solutions with citric acid (3 μm h^{-1} at pH 12.75) [3] and Quadrol (*N,N,N',N'*-tetrakis(2-hydroxypropyl)ethylenediamine) (4 μm h^{-1} at pH 13.0) as Cu(II) ligands [4]. Also rather high plating rates have been documented recently using novel ligands such as 4-hydroxypyridine-2,6-dicarboxylic and pyridine-2,6-dicarboxylic acids as the Cu(II) ligands – copper plating rates with these ligands reached 2.8 μm h^{-1} (pH 13.0) and 3.9 μm h^{-1} (pH 12.7) [17]. The use of L-tartrate and DL-tartrate was also investigated: the maximum plating rate of only about 1 μm h^{-1} (pH 13.0) was observed in solutions with L-tartrate, whereas it reached ca. 3.5 μm h^{-1} (pH 12.5) when using the racemic mixture of DL-tartrate [4] – the documented data differ somewhat from the data presented in this paper and could be partially explained by the insufficient purity of the used tartrates [4]. Thus, tartrates-containing electroless copper plating solutions give rates of copper deposition that are comparable to other ligands. Only D-tartrate could be separated from the ligands described – the use of this ligand results in the lowest plating rates than all obtained.

The process of electroless copper deposition from tartrates-containing solutions occurs at –300 – –430 mV, i. e. at relatively positive open circuit potentials (E_{mix}). More negative values of E_{mix} were observed in systems with saccharose [11] (up to ca. –700 mV), citric acid (up to ca. –600 mV) [3] or 4-hydroxypyridine-2,6-dicarboxylic and pyridine-2,6-dicarboxylic acids as the Cu(II) ligands (up to ca. –740 mV) [17]. Usually the values of E_{mix} are in the range from –240 to –500 mV for systems with other ligands [5]. It should be mentioned that the values of E_{mix} for L-tartrate and DL-tartrate containing systems measured in our experiments (Table 1, Fig. 5) are in good agreement with the given ones [5].

Usually the surface roughness factor (R_f) of electrolessly deposited copper coatings exceeds those of Cu electroplated from an acid copper(II) sulfate bath (R_f ~ 1.5). Previously, copper coatings with the highest R_f values were obtained from solutions containing the following Cu(II) ligands: pyridine-2,6-dicarboxylic acid (R_f = 124) [17], 4-hydroxypyridine-2,6-dicarboxylic acid (R_f = 35 [17]), Quadrol (R_f = 23) [4] and saccharose (R_f = 25) [11]. In the case of use of EDTA, L-tartrate and DL-tartrate, the values of R_f are lower and do not exceed 18 [6]. Our experiments show that surface roughness factor values of copper coatings obtained using D-, L- and DL-tartrate in this work are in the range from 1.6 (very close to electroplated copper) to 8 (Table 1, Fig. 4), and are comparatively smooth in most cases.

The overpotential values of copper electrode obtained for D-, L- and DL-tartrate containing electroless copper solutions are in the range from –160 to –310 mV (Table 1 and Fig. 7) and are in good agreement with data documented earlier for L- and DL-tartrate [5]. It can be noted that the process of the electroless copper deposition using the mentioned ligands proceeds at a relatively low overpotential, since in the case of sacharose it reaches –520 – –570 mV [11], for pyridine-2,6-dicarboxylic acid it was determined to be –600 mV [17]; only in the case of Quadrol the overpotential was found extremely low (ca. –50 mV) [4].

Concerning environmental aspects of the use of tartrates, it is worth noting that copper recovery from the used electroless copper plating solutions containing D-, L- or DL-tartrates as Cu(II) ligands is much less complicated than for solutions using conventional ligands such as EDTA or Quadrol, since the Cu(II) complexes with tartrate can be decomposed by simply lowering the solution pH up to acidic conditions (with some technological peculiarities). The remaining tartaric acid is environmentally benign, i. e. it does not form stable complexes with heavy metals under natural conditions and it is easily biodegraded.

CONCLUSIONS

This study has shown the possibility of using of all investigated isomers of tartaric acid, namely L-tartrate, D-tartrate and the racemic mixture of DL-tartrate, as Cu(II) ligands in electroless copper plating systems. The autocatalytic reduction of Cu(II) by formaldehyde from solutions containing the mentioned ligands begins at about pH 12.

The process of electroless copper deposition from tartrates-containing solutions occurs at relatively positive open-circuit potentials (from ca. –300 to ca. –430 mV). Overpotential values are also comparatively low (from ca. –160 to ca. –310 mV) for electroless copper plating solutions.

A correlation among copper plating rates and surface roughness values of the copper deposits formed has been established.

For all coating obtained the values of formaldehyde anodic oxidation current peak rise with increase in solution pH from 12.0 to 13.0.

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EKOLOGIŠKŲ LIGANDŲ PANAUDOJIMAS CHEMINIO VARIAVIMO SISTEMOSE: PALYGINAMASIS CHEMINIO VARIAVIMO TYRIMAS CU(II) LIGANDAIS NAUDOJANT D-, L- BEI DL-TARTRATUS

Santrauka

Nustatyta, kad visi tirti vyno rūgšties izomerai, t. y. D-tartratas, L-tartratas ir racematinis mišinys DL-tartratas, šarminėje terpėje sudarantys pakankamai patvarius kompleksus su vario(II) jonais, yra tinkami ligandai vario(II) kompleksinimui šarminiuose (pH > 12) cheminio variavimo tirpaluose. Ištirta vario(II)-tartratinių kompleksų (su minėtaisiais izomerais) redukcija hidratuotu formaldehidu, apibūdintas gautųjų vario dangų šiurkštumas. Optimaliomis proceso vykdymo sąlygomis kambario temperatūroje per vieną valandą gali būti nusodintos kompaktiškos nuo 1 iki ~3 μm storio vario dangos. Cheminio variavimo tirpalai buvo stabilūs – jokių Cu(II) redukcijos tirpalo tūryje požymių nepastebėjome. Gauti rezultatai palyginti su duomenimis, gautais sistemose su kitokiais ligandais. Aptartos ir galimos pusiausvyros tirtuose tirpaluose.